Controlling Cr(VI) in Leather: A Review from Passive Prevention to Stabilization of Chromium Complexes

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Abstract

The Cr(VI) content in leather has garnered much attention in today's world of increasingly stringent environmental and safety regulations. In addition, the European Union (EU) countries have zero tolerance policies. For chromium-tanned leather, there is a risk of converting trivalent chromium into the hexavalent form in the processes of production, storage, transportation and usage. In this article, the routes for the occurrence of Cr(VI) are briefly analyzed, and the various types of Cr(VI) control technologies in leather manufacturing processes are reviewed.

One control technology is passive PREVENTION, which could inhibit the hexavalent chromium to some extent through the addition of antioxidants and reducing agents, but it might not fundamentally solve the hexavalent problem.

In contrast, CONSOLIDATION technologies to improve the stabilization of chromium complexes could play critical and responsible roles to effectively prevent the emergence of hexavalent chromium in leather. Several proposals are addressed for the control of Cr(VI) in leather, and CONSOLIDATION technology is determined to be more important than PREVENTION technology.

In addition, a new viewpoint is presented to completely solve the problem based on the stability of Cr^{3+} complexes. Taking the amount of Cr(VI) as a quantitative indicator, the mechanisms and key technologies for the effect of specific coordinating compounds (ligands) on the stability of Cr^{3+} to prevent Cr(VI) formation would be recommended for further study toward.

Introduction

More than 90% of the leather in the world is processed using chromium salts because of the facile technology, the reliability of the process, and the high technological and operational properties of the finished leather.[1] However, since 1994 when traces of hexavalent chromium were first detected in leather products, chromium-tanned leather has attracted increasing attention[2] because hexavalent chromium can cause cancer, skin allergies, and liver and kidney necrosis.[3] The European Union (EU) countries even have zero tolerance policies.[4] Nevertheless, a chromium salt in its trivalent form (basic chromium sulfate, $Cr(OH)SO_4$) is used in tanning. Chromium-tanned leather imparts an excellent hydrothermal stability due to the stable Cr^{3+} complexes. The stable cross-linked structure is formed through coordinate bonds between Cr^{3+} and the side-chain ionized carboxyl groups of collagen proteins.[5] Cr^{6+} is not used in any step of leather manufacture; therefore, the emergence of hexavalent chromium in leather products should be explained.

Numerous studies concentrating on the processing,[6,7] auxiliaries,[3,6,8,9] temperature,[8,10] photoaging,[11] humidity,[12,13] and other factors in the leather manufacturing process have been performed to understand the formation of hexavalent chromium. It was found that peroxide and free radicals (ROO·, RO· and ·OH) generated by unsaturated fatliquoring agents, photoaging and temperature, play important roles in promoting the Cr^{3+} oxidation reaction.[15] Therefore, many antioxidants and reducing agents have been used in leather processing with the goal of blocking the free-radical chain oxidation or reducing the produced Cr^{6+}. However, it is not entirely clear what factors contribute to the emergence of Cr^{6+}. This passively controlled technology only achieves PREVENTION, and its effect is limited. Passive prevention cannot fundamentally solve the hexavalent chromium problem.

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Manuscript received February 17, 2017, accepted for publication April 19, 2017.

Based on thermodynamic and kinetic principles, the stability of the compound itself is the most fundamental factor to determine whether a redox reaction occurs;[16] this is also true for the Cr^{3+} complex. Trivalent chromium exists in a free, mono-coordinate or multi-coordinate state in leather.[17] Therefore, it is assumed that the conversion of trivalent to hexavalent forms may be primarily associated with the chemical instability of Cr^{3+} in leathers, which has been verified by Gong *et al.*[18] Cr^{3+} in unstable coordination states was easily converted into Cr^{6+} in high pH environments. A higher percentage of the deficiently coordinated Cr^{3+} in the belly leads to more Cr^{6+} after aging compared with that in the butt.[18] Therefore, many high exhaustion auxiliaries were explored to enhance Cr^{3+} coordination by increasing the Cr^{3+} combinational points with collagen. Thus, technology for CONSOLIDATION to improve the stabilization of Cr^{3+} complexes could play a critical and responsible role in effectively preventing the emergence of hexavalent chromium in leather.

Based on the above two aspects, Cr(VI)-control technologies have been recognized in detail and reviewed systematically to prevent the generation of Cr(VI) in leather. In addition, it is expected that this review will attract great interest for research and development in this area.

1. Passive prevention of Cr(VI)

It was indicated that Cr^{6+} formation was mainly caused by hydroxyl radicals from a series of radical reactions derived from α-H autoxidation. These external conditions, such as unsaturated fatliquoring agents, photoaging and temperature, could cause the production of free radicals R· in leather, which subsequently generate the peroxide radicals ROO·, ·OH and RO· by reaction with oxygen. The specific mechanism[14] is as follows.

Chain Initiation:

$RH \rightarrow R\cdot + H$

Chain Growth:

$R\cdot + O_2 \rightarrow \mathbf{ROO\cdot}$, $\quad ROO\cdot + RH \rightarrow ROOH + R\cdot$,

$2ROOH \rightarrow ROO\cdot + \mathbf{RO\cdot} + H_2O$, $\quad ROOH \rightarrow \mathbf{RO\cdot} + \cdot OH$,

$RH + \cdot OH \rightarrow R\cdot + H_2O$, $\quad \mathbf{RO\cdot} + RH \rightarrow ROH + R\cdot$

RH represents collagen, synthetic tanning agents, fatliquoring agents or dyeing agents.

Adding many antioxidants could prevent the formation of Cr(VI) due to the following single or joint actions:[19] (1) hindering chain growth (antioxidants such as some synthetic antioxidants and vegetal tanning extracts) by providing hydrogen to ROO· and terminating the reaction of ROO· and RH; (2) hindering the continued oxidation of RH (antioxidants such as polyphenols) by providing hydrogen to R· and then restoring RH to its original state; (3) chelating with metal ions (antioxidants such as polyphenols and phytic acid); (4) blocking the peroxidation chain reaction (antioxidants such as tocopherol and ascorbic acid) by capturing all free radicals, such as R·, ROO· and RO·; and (5) other actions such as using an ultraviolet absorber. Moreover, reducing agents such as sulfur compounds could convert chromium from the hexavalent to the trivalent form due to their strong reducibility.

However, antioxidants or reducing agents show variations in inhibiting influences on Cr(VI) formation due to their various molecular structures and conformations, leather manufacturing conditions, aging conditions, etc. Two or three types of antioxidants have also been mixed together for the desired purpose.

1.1 Sulfur Compounds and Small Molecule Phenols

Some small molecule compounds could decrease the amount of Cr^{6+} in leather, but Cr^{6+} was not eliminated, especially after accelerated aging. Sodium thiosulfate has been the most effective compounds among sulfur and phosphonium compounds, and it decreased Cr^{6+} to 1 mg/kg.[21-23] Sodium bisulfite and tetrakis(hydroxymethyl)phosphonium sulfate reduced Cr^{6+} well below 3 mg/kg.[20] Synthetic antioxidants, such as bibutylhydroxytoluene (BHT) and butylhydroxyanisole (BHA), did not achieve the expected result.[21,25] Therefore, antioxidants (BHT, BHA and citric acid) were combined to produce an obvious effect that reduced the amount of Cr^{6+} to 2.9 mg/kg.[21] In addition, the amount of Cr^{6+} in crust leather was reduced to less than 5 mg/kg with 1.5% hydroquinone.[24]

1.2 Vegetal Tanning Extracts

Vegetable tannins (condensed and hydrolyzable) had a strong inhibitory effect on the Cr^{3+} oxidation in leather. The greater number of hydroxyl groups on the single-ring polyhydroxy phenol resulted in a stronger inhibitory effect of α-H oxidation. With the same number of hydroxyl groups on the single-ring polyhydroxy phenols, o-hydroxy phenol had a stronger inhibition than that of p-hydroxy phenols.[26]

Some vegetable tannins, such as bayberry, mimosa, quebracho, sumac, tara, valonea, chestnut, larch and myrobalan, are used in the purpose. Consequently, bayberry tannin extract was found to be a more effective tannin than tara, which decreases the amount of Cr^{6+} to less than 3 m/kg.[23] Valonea and henna have lower inhibitory effects than the other mentioned tannins.[29] Gallotannins (myrobalan, tara and sumac) have the highest power for antioxidant activities among the hydrolyzable tannins.[15,27] However, vegetable tannin does not easily permeate into leather due to its high molecular weight. Some modified vegetable tannin extracts with lower molecular weights were studied, e.g., the isolated components of bayberry and tara tannin extracted by ultrasonic waves[30], the esterification-modified of valonia extracts,[31] and the amphoteric- and sulfuric-modified product of black wattle extract.[32] These modified extracts reduced the amount of Cr^{6+} to 3 mg/kg in the crust.

In addition, the degradation products of hydrolyzable tannins, such as gallic acid (GA), ellagic acid and tannin, have a remarkable effect on Cr^{6+}, even after accelerated aging. GA reduced the amount of Cr^{6+} to less than 5 mg/kg, even after heating and exposure to UV irradiation for 3 days in leather,[33] and its derivatives, TBM (N,N,N’’’-(1,3,5-triazine-2,4,6-triyl) tris(3,4,5-trihydroxybenzamide)), decreased the amount of Cr^{6+} to less than 3 mg/kg.[24] Nevertheless, the antioxidant capacity of ellagic acid is greater than that of GA;[34] 2% ellagic acid could reduce the amount of Cr^{6+} to less than 3 mg/kg, even under irradiation treatment.[35] In addition, the amount of Cr^{6+} was reduced to less than 3 m/kg with 3% tannin.[28]

1.3 Other Natural Polymers

It was shown that α-tocopherol (vitamin E) and mixed tocopherols produced from a renewable source, such as soybeans, could significantly improve the UV and heat resistance of leather.[36] Vitamin E has a strong ability to prevent the formation of Cr(VI) with a dosage of 4%. Phytic acid is more effective than vitamin E but worse than ascorbic acid (vitamin C).[21] Although vitamin C can inhibit the Cr^{3+} oxidation to some extent, it still could not completely inhibit the oxidation after accelerated aging.[21,24,25,27] Meanwhile, the essential oil of origanum minutiflorum as a fungicide can prevent Cr^{6+} formation in leather.[37]

The protein filling agent prepared from bovine hair (HPFA) possessed a remarkable inhibitory effect on Cr^{3+} oxidation over the range of 20°C to 100°C.[38] Collagen peptides (CPs) with low molecular weights (MW approximately 10,000) could considerably reduce Cr^{6+}.[39] However, individual treatment with the material did not result in complete inhibition, the combined treatment with BHA, vitamin C and CPs, achieved a satisfactory effect, even in heat-aged leather.[25]

2. Stabilization of chromium complexes

The kinetics of the redox reaction are complicated, but it is clear that there is a dependency on the redox electrode potential of the metal ion. As a metal ion complex is formed, the redox electrode potential of the metal ion would change, consequently altering its redox stability. In terms of the influence of ligands on the Cr^{6+}/Cr^{3+} electrode potential, $E=1.33+0.059\times(\lg\beta_{(3+)}-\lg\beta_{(6+)})$, a ligand with stronger coordinating property to Cr^{3+} has a larger lgβ(3+).[40] A higher Cr^{6+}/Cr^{3+} electrode potential E indicates that it is more difficult to oxidize the Cr^{3+} compound by external conditions. Furthermore, a Cr^{3+} complex with a stronger coordinating property is particularly important for inhibiting Cr^{3+} oxidation in leather.

The chromium-tanning mechanism involves chromium salts ($Cr(OH)SO_4$) undergoing hydrolysis, polymerization of the hydroxyl groups in water, and forming positive multicore Cr^{3+} complexes that are attracted to the negative side-chain carboxyl groups of collagen. Thereby, strong coordinate bonds between Cr^{3+} and carboxyl groups are generated.[5] However, approximately only one-tenth of Cr^{3+} is involved in crosslinking, and approximately only one-sixtieth of the carboxyl groups of collagen forms complexes with Cr^{3+} in a conventional manner.[41] Hence, the multi-point binding rate of Cr^{3+} complexes in leather is low.

High exhaustion auxiliaries can improve the Cr^{3+} coordination ability with collagen by changing the traditional ligand structure of the chromium complex in leather. The rich terminal carboxyl groups, such as aldehyde acids, oxazolidine and polymer compounds, contribute to achieve more stable coordination with Cr^{3+}, as shown in Figure 1.

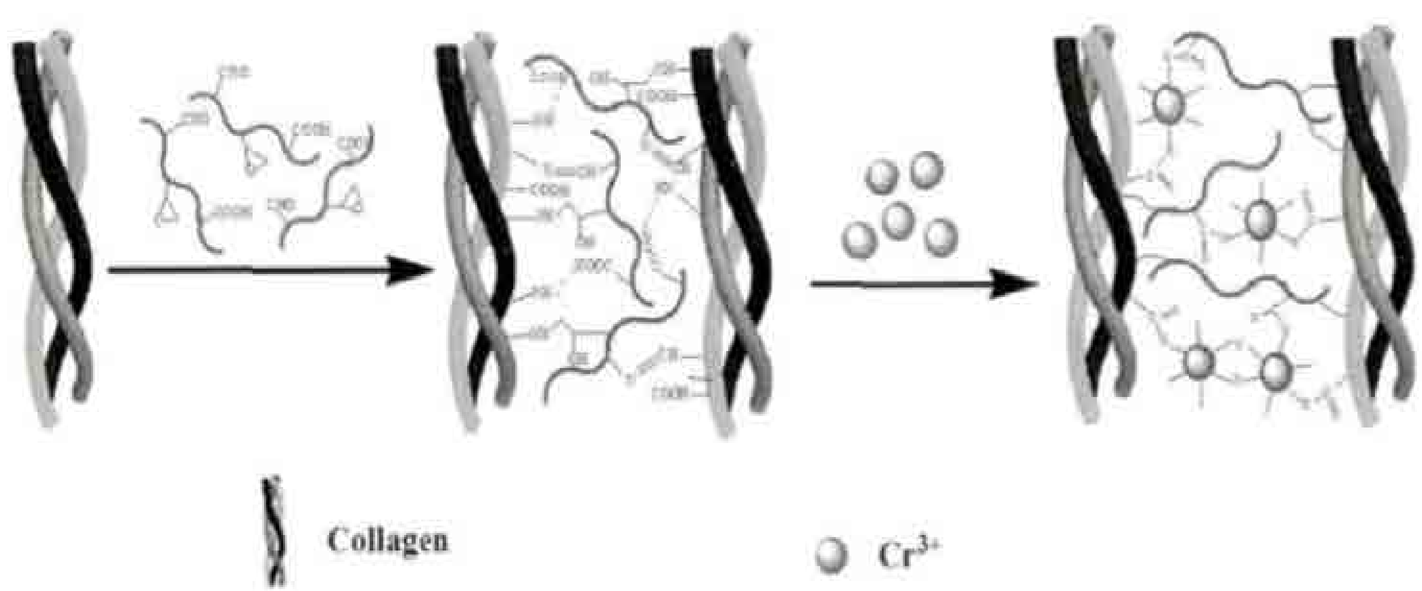

Figure 1. Proposed interaction mechanism of the high exhaustion auxiliaries of chrome with collagen and Cr^{3+}.

2.1 Small Molecule Compounds

2.1.1 Dicarboxylic Acids And Polycarboxylic Acid

Hexavalent chromium elimination agent, a mixture of polycarboxylates, polycarboxy polymer, organic anhydride and some alkaline agents, could completely remove Cr^{6+} in leather, even after UV or high-temperature aging, and no hexavalent chromium could be detected by aging for 72 h.[44] The same effect was achieved when treating the specific material with reducers and metal chelating agents, as shown by Gong *et al.*[18] Phthalic acid pretanning agent (HTPA) resulted in a significant increase in chromium uptake and higher shrinkage temperature, thus increasing the stability of Cr^{3+} complexes.[43]

2.1.2 Aldehyde Acids

Multiple aldehyde acids increased the shrinking temperature to above 100°C and decreased the chromium content of effluent to less than 0.3 g/L.[46] A glyoxylic acid assistant agent, synthesized by the Michael addition reaction, increased the properties of the combination capacity of chromium and collagen, and the absorption of Cr^{3+} reached nearly 90.0%.[47] An aldehyde acid tanning agent with CHO and COOH group, also enhanced the absorption and crosslinking of Cr^{3+}.[45]

2.1.3 Oxazolidine

Bicyclic oxazolidine showed a better performance than did monocyclic ones at reducing the chromium emission level.[48] An oxazolidine chromium-tanning auxiliary (OXD-I), which contains carboxyl, hydroxyl and tetra-amino groups, decreased the Cr_2O_3 content in wastewater to 0.18 g/L when its dosage was 2%, and the chromium absorptivity reached 97.0%.[49,50] The oxazolidine derivative with carboxyl group and an oxazolidine ring, increased the maximum adsorption capacity of Cr^{3+} from 41 mg/g to 143 mg/g.[51]

2.2 High-Molecular-weight Polymers

2.2.1 Resin Polymers

Resin polymers are mainly composed of polycarboxylic acid polymers. An amphiphilic acrylic copolymer, synthesized by lauryl acrylate and acrylic acid, had a greater impact on the binding of chromium in collagen and enhanced the thermal stability.[52] The cationic acrylic auxiliary tanning agent increased the absorption of Cr^{3+} to more than 90.0%.[53] An advanced polymeric material (PMAA) based on acrylic acid promoted a 5-fold intensification of tanning and increased the fixation and chromium exhaustion to 17.5% to replacing the traditional pickling step.[55]

Diisocyanates qualify as tanning agents due to their strong tendency to crosslink collagen molecules by reacting with amino groups. A multi-carboxyl polyurethane increased chromium exhaustion to more than 85.0% and decreased the Cr_2O_3 content below 2.22 mg/kg, and with an increase of the multi-carboxyl polyurethane content, these effects were enhanced.[56] In addition, three types of blocked-waterborne polyurethane (B-WPU) oligomers could improve the chromium absorption and decrease Cr_2O_3 in the effluent.[57] A waterborne dimethylolpropionic acid-diisocyanate adduct (WDDA) enabled the chromium uptake to reach 90%.[58]

2.2.2 Hyperbranched Polymers

Due to their strong coordination ability, fast speed, large ion capacity and high selectivity, hyperbranched polymers have been developed as potential masking agents or tanning auxiliaries in chrome tanning.[59,60] As shown in Figure 2, coupled with its highly branched structural characteristics, the control of the molecular weight and the type and quantity of molecular terminal functional groups could improve the coordination of a hyperbranched copolymer with Cr^{3+}. Consequently, these polymers effectively enhanced the combination of chromium-tanning agents and collagen fiber. In terms of the Cr^{3+} complex stability against alkali conditions and oxidation, this polymer radically reduces the formation of Cr(VI) in leather.

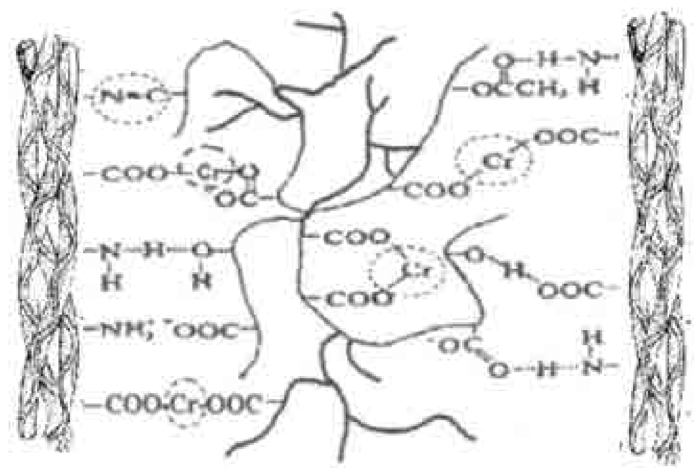

Figure 2. Proposed mechanism of hyperbranched polymers with collagen and Cr(III).

Carboxyl-terminated hyperbranched polymers. The waterborne hyperbranched oligomers named HBP-1x (where HBP-1x is the general name for this series of products) have better effects on the absorption rate of chromium (78%) with the addition of basifying agents [60-62] A hyperbranched polymer based on acrylic acid also served as a better dispersing and fixing agent for basic chromium sulfate. The absorption rate of chromium reached more than 70% under any conditions.[62] An amount of 0.02 g/L of Cr_2O_3 in the effluent was obtained with 5.0% waterborne epoxy combined with 3.0% chromium salts.[65]

Amino-terminated hyperbranched polymers. A multifunctional amino-terminated hyperbranched poly(amidoamine) (HPAM) improved the fixation and exhaustion of chromium as a pretanning agent.[66] Furthermore, chromium exhaustion was 99.8% with 5.0% HPAM, and the residual chromium in the tanning bath decreased to 2.15 mg/L.

Phenol hydroxyl-terminated hyperbranched polymers. A hyperbranched polyurethane polymer had good performance for inhibiting Cr^{6+}.[67] A novel hydroxyl-terminated hyperbranched polymer (HTHP) reduced Cr_2O_3 in the chromium-tanning effluent from 1.42 g/L to 0.60 g/L.[69] A hyperbranched polymer as a pretanning agent reduced the Cr_2O_3 content in the tannery effluent to 45%.[70] Hyperbranched poly(amine-ester) was reacted with maleic anhydride to obtain a new hyperbranched polymeric (HP) chromium-tanning auxiliary with various functional groups.[71] When 2% HP was used in chromium tanning, the chromium absorptivity reached over 95%.

2.2.3 Bioadditives

Some green, renewable, biodegradable and less pollution-prone substances, such as starches, chitosan, enzymes, collagen and GA, have been developed and applied to facilitate cross-linking with chromium.

A modified starch as a pretanning agent improved the binding of Cr^{3+}. The Cr_2O_3 content in the effluent was reduced to 0.26 g/L.[74] The modified chitosan was used for intensifying the process of chrome tanning while simultaneously increasing the shrinkage temperature and chromium sorption capacity.[75,76] Microbial transglutaminases (MTG) also significantly improved the chromium exhaustion and effectively decreased the amount of Cr_2O_3 in the effluents to 0.15 g/L.[77] Silk hydrolysate applied before and after tanning caused the chromium absorption to reach 95.0%.[78]

Collagen hydrolysate, extracted from protein-based wastes, can be modified by introducing specific targeting groups, such as aldehydes, carboxyls, hydroxyls and other active groups. A modified collagen hydrolysate reduced the chromium content of the tanning solution to less than 18.2%.[85] Acid hydrolysis of horn meal (obtained from the raw horns of slaughtered cattle and buffaloes) yielded a mixture of water-soluble and low-molecular-weight peptides.[86] These peptides reacted with Cr^{3+} to yield a product that exhibited high exhaustion of the chromium bath (above 92%).

Kanagara also performed a series of studies on modified collagen hydrolysate as a chromium exhaustion aid through a three-step "chromium adsorption–diffusion–reaction with collagen" process.[79-84] Fleshing hydrolysate, prepared from limed fleshings, improved chromium uptake to 91.5%.[80] The novel nanoparticle dispersion copolymer in aqueous medium was used as a high-exhaustion chromium aid to obtain 94.0% exhaustion of chromium.[82] Optimal adsorption of 96.0% of chromium in the first cycle and 98.9% in the second cycle was observed with 6% graft copolymer, which was synthesized from chromium shaving waste and polyethylene glycol (PEG).[83] A novel graft copolymer adsorbent, which was prepared from collagen hydrolysate, was employed to enhance the uptake of Cr^{3+} to 94.0%.[84]

A greener approach based on GA for chromium tanning was attempted.[87] GA enhanced Cr^{3+} uptake to more than 93%.

2.4 Others

Some inorganic salts facilitated chromium tanning. An aluminum-based syntan (Alutan) increased the uptake of chromium over the range of 84 to 94%.[88] The chromium in the effluent was reduced below 0.5 g/L through sequential tanning with 4% organic-acid-masked aluminum (HET), 4% chromium tanning agent and 0.6% HET. Moreover, the Cr^{6+} content in the finished leather was less than 3.0 mg/kg, even when using the unsaturated fatliquoring.[89]

3. Summary

The safety and ecological properties of leather products as daily consumer goods have resulted in widespread concern from governments and consumers. Cr(VI) in leather has garnered substantial attention from leather scientists. Although passive PREVENTION can inhibit hexavalent chromium to some extent, antioxidants and reducing agents have been unable to fundamentally resist the high-intensity conditions of UV exposure and heat aging. Theoretically, the generation of hexavalent chromium could be completely inhibited by increasing the electrode potential of Cr^{6+}/Cr^{3+}. Therefore, CONSOLIDATION technology to improve the stability of chromium complexes could play a critical and responsible role to effectively ensure that Cr^{3+} is stabilized in leather. However, the actual prevention of Cr^{6+} via high exhaustion auxiliaries for chrome tanning has been rarely used in practice. This parameter is mainly characterized by the percent exhaustion of chromium and chromium content in the waste, which does not truly reflect the stability of chromium in the interior of the leather. Therefore, the following topics are recommended for further study from the viewpoints of economy and technology.

1. Regarding the stability of the Cr^{3+} complex, the coordination reactions of specific coordinating compounds (ligands) with Cr^{3+}, as well as the stability, structure and properties of the Cr^{3+} complexes formed, should be studied with the goal of presenting compounds (ligands) that enable better Cr^{3+} stability.

2. Using the amount of Cr^{6+}, the absorption properties and the finished leather quality as quantitative indicators, the mechanisms and key technologies of ligands to stabilize Cr^{3+} and prevent the formation of Cr^{6+} should be studied. Therefore, ligands that best stabilize Cr^{3+} would be selected.

3. The relationship between the aging conditions and the generated Cr^{6+} would be studied to understand the kinetics of the oxidation of trivalent to the hexavalent form.

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