SYNTHETIC ORGANIC TANNING SYSTEM

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Even the optimization of common chromium tannage, and combined tannage with chromium and other tanning materials have led to outstanding results related to the lowered pollution level in effluents and sludge, the problem has not been solved wholly. The single solution for this problem is finding out an environmentally friendly alternative to chromium tannage. This work also is within the above line, aiming to obtain wet-white leather by an organic tanning process in order to reduce chromium in tannery effluent.

Keywords: organic tannage, wet white, synthetic tannage.

INTRODUCTION

Chrome tanning is the most common type of tanning in the world. Chrome tanned leathers are characterised by top handling quality, high hydro-thermal stability and excellent user properties. Chrome waste from leather processing poses a significant disposal problem. It occurs in three forms: liquid waste, solid tanned waste and sludge. In most countries, regulations governing chrome discharge from tanneries are stringent. Today, all tanneries must thoroughly check their waste streams. Chrome discharge into those streams is one of the components that has to be strictly controlled.

The environmental impact of chrome waste from tanneries has been a subject of extensive scientific and technical dispute. Statutory limits have since been set for chrome discharge and disposal, and relevant guidelines have been drawn up throughout the world. Given the close correlation between chrome tanning and the environmental impact of leather processing, auditing the efficiency of processing operations takes on prime importance.

Conventional chroming process generally involves in pickling, chroming and basifying, and there are several defects existing in the process (Sykes 1981, Germann 1995): i) 8-10% salt and 1.0-1.2% sulfuric acid were used in pickling, which results in higher contents of chlorides, sulfates and chemical oxygen demand (COD) in the effluent. ii) The uptake of chromium in conventional chroming is lower (70-80%), a considerable amount of chromium left in the effluent may result in environmental problems(Ludvik 1997). iii) A great deal of chrome containing solid wastes such as splittings and shavings are produced, which is certainly difficult to be degraded and harmful on the environment if discharged directly (Tao Zhang et al., 2009).

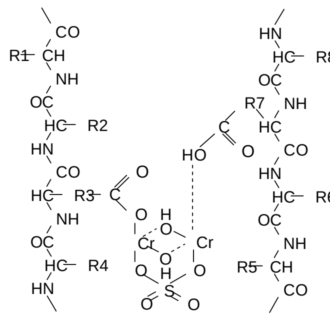

Figure 1. Collagen-chromium (III) compounds – crosslinked

Much criticism has been directed towards the use of chromium salts in leather tanning, but it has to be borne in mind that chromium can occur in different oxidation states and its compounds behave differently. Most chromium(VI) compounds are highly toxic and classified as MAK III A 2 carcinogens, but chromium(III) is an important trace element in man and animals.

Chromium compounds are, or at least used to be, one of the most common causes of occupational skin disorders. Chromium(III) is not regarded as being sensitizing, because it does not readily penetrate the skin, but water-soluble chromium(VI) compounds penetrate the skin very easily. Chromium(VI) is then reduced intracutaneously to trivalent chromium, which enables it to react with the proteins in the skin and trigger an allergic reaction.

The issue of chrome is perhaps one of the most debated issues between authorities and the tanning industry because of the difference in opinion about the toxicity of chromium (III) salts used in the tanning industry. The tanning industry has the view that the chromium (III) tanning agent is not toxic and can be compared with table salt. Authorities opinion is that chromium (III) should be considered toxic, especially for aquatic life. What is agreed is that chromium (VI) is much more toxic than chromium (III). The toxic mechanism of action differs for hexavalent versus trivalent chromium. Hexavalent chromium causes cellular damage via its role as a strong oxidising agent, whereas trivalent chromium can inhibit various enzyme systems or react with organic molecules. Chromium (III), the naturally occurring form, has low toxicity because it is non-corrosive and passes poorly through membranes, but chromium (VI) is highly toxic because it has strong oxidation characteristics and passes readily through membranes.

Chrome is mentioned in list 2 of the Annex to Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Tannery wastes containing chromium are not included in the European Hazardous Waste List on the basis that the wastes do not possess the characteristics necessary for classification as a hazardous waste (COTANCE, 2002).

Despite the fact that chromium has been under pressure from some regulatory authorities, the extent of substitution of chromium tanning agents has been limited. The main reason for this is that chromium is the most efficient and versatile tanning agent available, and it is relatively cheap.

These practical and operational constraints have resulted in attempts to find an alternative to chromium (III) tanning (German H.P., 2010) for the production of free-of-chrome (FOC) leather, whilst retaining the mineral character in leather. Accordingly, Al (III) (Hernandez J.H., 1983; Hancock R. A. et al., 1980), Zr (III), Ti (III & IV) (Bi Yu Peng et al., 2007), Kleban, M., US Pat, Appl. No. 200601151738, their mixed salts (Covington A.D., US Patents 4563156, 4731089) and most recently nano-silicates (Liu, Y, et al 2010) and sodium waterglass were tested as effective partial or total replacement tanning agents or for the production of a reversibly tanned new intermediate semi-processed product and commodity: “wet-white” or “wet-stabilised” leather. Overall metal ion complexes have some affinity for protein, but when applying the criteria of adequate reactivity colour, availability, cost and toxicity eliminates nearly all of the commercially available agents as viable options.

Syntans, Resins, and Polyacrylates are agents used alternatively or in addition to chrome and vegetable tannins.

Previous research studies demonstrated that using oxazolidine (Roig et al., 2011) (Figure 2) or resorcinol tanning agents (Hiu et al., 2009) (Figure 3) combined with other (vegetable or synthetic agents) allows for the obtaining of quality leathers that can be used by footwear and upholstery industries.

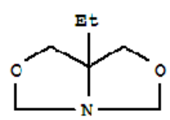

Figure 2. Oxazolidine E

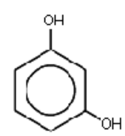

Figure 3. Resorcinol

Oxazolidines

Oxazolidines (Angus Chem. GmbH) are saturated heterocyclic compounds prepared by reacting primary amino alcohols with formaldehyde. Monocyclic or bicyclic oxazolidine ring structures are formed depending on the choice of starting chemicals, it is therefore possible to synthesize a variety of oxazolidines from different amino alcohols. Oxazolidines are highly useful chemicals for a wide variety of applications: corrosion inhibitors, emulsifiers, diluents or tanning agents. The oxazolidine marketed for use as tanning agents are water soluble compounds, compatible with most chemicals normally used in tanning operations and can be introduced at several points in the tanning process.

The capacity of the Oxazolidine E for tanning leather is based on the formation of a reaction intermediate due to:

- the protonation of oxygen of each ring in acid medium, which weakens the C-O bond or,

- the oxazolidine rings opening caused by hydrolysis in an acid medium to provide an intermediate with two N-(hydroxymethyl) groups, and the subsequent nucleophilic attack of the collagen amino groups to this intermediate specie (Figure 4).

Leathers tanned with chromium salts have a high stability, determined by a shrinkage temperature (Tg) over 100°C, while the leathers tanned with oxazolidine alone reach shrinkage temperatures of below 75°C. It is therefore necessary to carry out the oxazolidine tanning in combination with synthetic or vegetable tanning agents to achieve higher shrinkage temperatures and obtain leather of comparable quality to the chrome tanned leather.

Resorcinol

Resorcinol is a diphenol which can be transformed into a prepolymer by Manich reaction with formaldehyde.

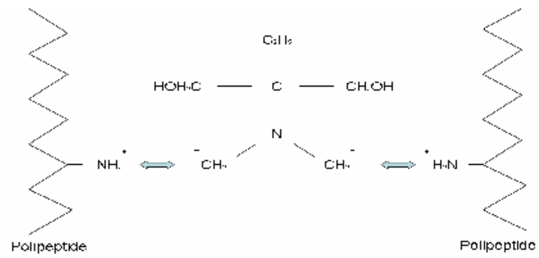

Figure 4. Collagen-oxazolidine crosslinked (Roig M. et al. 2011)

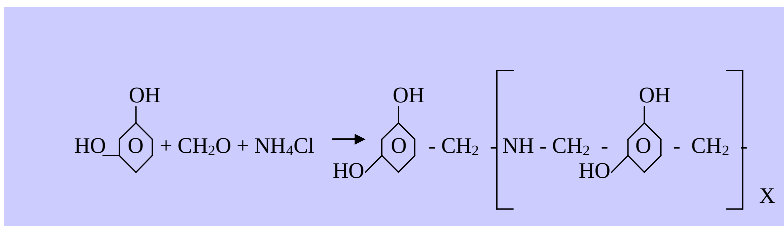

Figure 4. Tanning agent based on resorcinol pre-polymer

Resorcinol – Oxazolidine E

Recent studies demonstrated that resorcinol-oxazolidine E treated collagen is more stable system than that with sequential combination tannages with the same materials. The study has demonstrated that oxazolidine E underwent ring opening to form the N-methylol intermediate and reacted with the hydrogen bonds of resorcinol to form Tanning Matrix. The Tanning Matrix then penetrated into the collagen fibres and by aggregation prevented the denaturation of collagen fibres of heating. The next reaction is the involvement of hydrogen bonds and hydrophobic interactions, and the aldehyde groups of oxazolidine E in reaction with basic amino acid side chains of collagen as the major force involved in stabilization of collagen. In this way, a multiple point combination tanning occurs with the Tanning Matrix creating a high level stabilization of collagen and high hydrothermal stability (Hui et al., 2009).

This model of reticulation of resorcinol-oxazolidine E with collagen is shown in Figure 6.

This paper present the results obtained from different tanning tests on cowhides, at a pilot scale, using oxazolidine, resorcinol prepolymer or oxazolidine-resorcinol combination as an alternative to traditional chrome tanning. It is presented the procedures followed, physical characterization of obtained leathers, as well as the impact of this technology on waste water and solid waste generated.

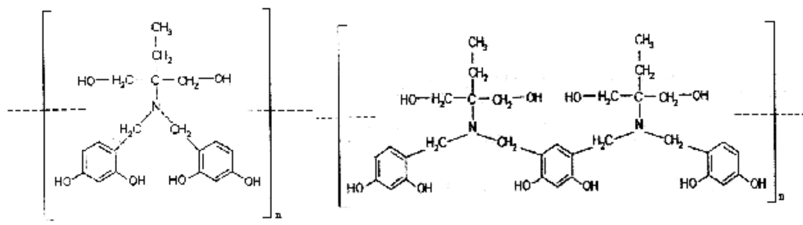

Figure 6. Reticulation model of resorcinol-oxazolidine E with collagen

MATERIALS AND METHODS

Salted cowhides were chosen as raw material for the chromium-free leather production for determining the effects of the newly synthesized leather tanning products. These newly synthesized organic tanning agents based on pre-polymers shown in Figures 2 and 3 were used as pre-tanning agents for this study (Platon et al., 2010).

The Figure 7 presents the Flow Chart for conventional and experimental processes and the Figure 8 presents the equipment for experiments at pilot scale.

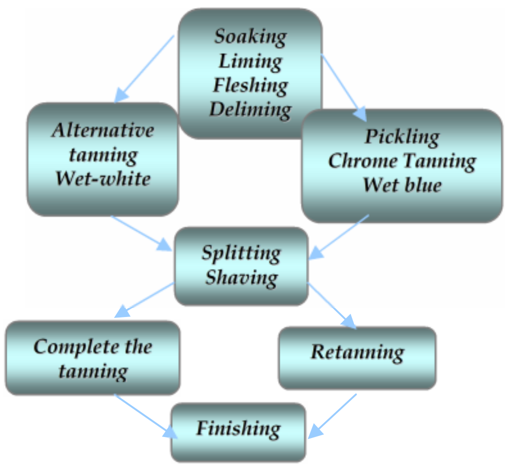

Figure 7. Flow Chart for conventional and experimental processes

EXPERIMENTAL

Wet salted cowhides were treated from soaking to bating as usual. The bated pelts were cut along the backbone line, left parts for conventional process, and right parts for the experimental ones. The chemicals employed in the experiments are of commercial grade, the chemicals used for analytical technique are of reagent grade.

Figure 8. Tanning drum used in pre-tanning tests on pilot scale

Experimental and conventional processes are provided as Table 1. As Table 1 showing, bated pelts were directly pre-tanned with oxazolidine E (Experiment E3). The bated pelts were of high pH value (6.8-7.0) and most active groups of collagen were exposed. Control sample was made using Chromium salts (Experiment C) on pickled pelts. The other experiments were conducted also on pickled pelts at 2.8-3.0 pH. Then the pre-tanned pelts were split and shaved.

Table 1. Conventional and experimental pre-tanning

Exp code	Process	Chemical	Time	$pH_{initial}$ /pH_{final}
C	Conventional chrome tanning on pickled pelts	8% Chromium salts (25% Cr_2O_3) + 10% sodium bicarbonate	8 hours	3.0-4.0
E 1	Pre-tanning with Oxazolidine E on pickled pelts	2 % Oxazolidine E	5 hours	3.0-4.8
E 2	Pre-tanning with Resorcinol and Oxazolidine E on pickled pelts	4% Resorcinol pre-polymer + 2% Oxazolidine E + 1% sodium bicarbonate	10 hours	2.8-4.8
E 3	Pre-tanning with Oxazolidine E on bated pelts	2 % Oxazolidine E	5 hours	6.8-8.5

The pre-tanned leathers were analysed for shrinkage temperature presented in the Table 2.

Table 2. Shrinkage temperature (Ts) of the pre-tanned leathers

No.	Experiment code	Shrinkage temperature, Ts, °C
1.	C (conventional)	102
2.	E1	70
3.	E2	72
4.	E3	68

In the Table 3 the characteristics of tanning effluents are presented.

Table 3. Characteristics of Tanning Effluents

No.	Characteristics	Conventional chrome tanning	Organic tannings experiments		
		C	E1	E2	E3
1.	Sulfates, mg/dm^3	31669	265	30000	3374
2.	Chlorides, mg/dm^3	34602	-	30005	5744
3.	Chrome oxie, g/dm^3	4377	-	-	-

RESULTS AND DISCUSSION

Results indicated that the highest Ts of combination tanning leathers is resorcinol pre-polymer-oxazolidine E in sequence. In course of resorcinol pre-polymer tanning first the tanning parameters were pH 3.0 and 4% dosage (based on weight of caw pelts), and the tanning parameters were pH 3.5 and 2% dosage when oxazolidine E as tanning agent. The Ts of pre-tanned leather with resorcinol-oxazolidine combination was 72°C (Experiments E2).

Pickling is a preliminary process for preparing hides for tanning, largely by adjusting the pH with acid and controlling the swelling with salt. Higher salt concentrations in the tannery effluent resulting from the conventional pickling process have been an environmental concern, leading to a trend in developing a salt-free pickling process. Additionally, failure to control the swelling of hides during this step would lead to damage or defects in the fibre. This not only impacts the subsequent tanning process, but also the final quality of the tanned leather. In this study of salt-free pickling process oxazolidine E was used and compared to a conventional acid/salt pickling process (Experiments E1 and E3).

The penetration of the new tanning agents reflected by Shrinkage temperature (Ts) was not only complete, but also uniform, assuring stabilization of the wet-white leathers for further mechanical or other chemical processing.

All characteristics of Chrome Tanning Effluent (experiment C) are higher than those of experimental organic tanning.

The benefits of the novel tanning system using oxazolidine or/and resorcinol as the pre-tanning agents are:

- no chromium in organic tanning effluents which make it easier and cheaper to treat;
- residual salt could be significantly reduced;
- because the system eliminates a pickle step, there is a reduction in strong mineral and organic acids use;
- the tanning process could be reduced by up to five hours;
- the shrinkage temperatures ranged from 68-72°C, depending on the substrate.

CONCLUSIONS

Oxazolidines and resorcinol can be used as tanning agents in several different ways as illustrated in this paper.

Combinations of oxazolidines with resorcinol can replace chrome tanning without sacrificing the physical and thermal properties of the tanned leather. Finally, with the use of oxazolidine, a more effective salt-free pickling process can be achieved and the environmental impact within leather manufacturing can be further reduced.

Since there was no chromium existed in the splittings and shavings, the wastes could be treated and reused more easily.

Acknowledgements

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