STUDIES ON TANNING WITH ZIRCONIUM OXYCHLORIDE: PART II DEVELOPMENT OF A VERSATILE TANNING SYSTEM

by

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ABSTRACT

Zirconium oxychloride, with suitable ligand environment has been found to be an effective tanning agent. Hydrothermal stability of about 95°C was obtained for the leathers treated with zirconium oxychloride masked with citric acid. The present investigation focuses on possible methodologies to improve the properties of leathers obtained from zirconium oxychloride tanning to suit different product mix through treatment with various co-tanning adjuncts. Exhaustion of zirconium was found to be greater than 80% in all tanning experiments. The zirconium oxychloride leathers post-tanned without neutralization exhibit better organoleptic properties compared to leathers post-tanned after neutralization. The post-tanning operations have been optimised to obtain both upper and garment leathers. Treatment of zirconium oxychloride leathers with silica produced fuller and smooth grained upper leathers whereas, pre-treatment with gluteraldehyde resulted in soft garment leathers. Properties of the leathers obtained are on par with the conventional chrome tanned leathers. Thus a tanning system based on zirconium oxychloride has the potential to be as versatile as chrome tanning systems, which produce leathers for different end uses.

INTRODUCTION

A viable alternative to chrome tanning is of interest to the leather industry mainly to eliminate or minimize the discharges of the chromium(III) in any form. Effective processes, which enable the production of leathers bearing similar properties to those of conventional chrome tanned stock requires features such as (a) high hydrothermal stability, (b) good light fastness, (c) low environmental impact, (d) versatility and (e) comparable cost.

Zirconium seems to be a potential tanning agent to replace chromium in tanning. Earlier attempts have been made to produce basic zirconium sulfate as tanning agent masked with organic ligands.[1,2] Zirconium salts are known to cause drawn grain leathers due to their ease of hydrolysis.[3] There are several reports on the use of sulphate salts of zirconium in tanning,[4,5] but the associated disadvantages are poor solubility, drawn grain and the necessity to employ a high acidic pH (<2.5) for tanning. One of the most soluble forms of zirconium salt available is zirconium oxychloride.

In our earlier work we have demonstrated the tanning capabilities of zirconium oxychloride at a higher pH in the presence of a different ligand environment.[6] Zirconium oxychloride in the presence of citric acid produced leathers with hydrothermal stability of 94 °C. The success of any tanning system lies in obtaining leathers for different end uses. This is one of the important criteria, which has made chrome tanning to be a dominant tanning system in the tanning industry. Present investigation focuses on the improvement of zirconium oxychloride-citrate system, so as to evolve a versatile tanning system, to produce leathers for different end uses. Zirconium salts are known for producing leathers of firm nature.[7] Thus, developing softer leather by using zirconium oxychloride is a challenging task and needs proper processing adjustments and appropriate auxiliaries. In order to improve the properties of leathers, studies on combination tanning of zirconium oxychloride with co-tanning agents like sodium metasilicate, gluteraldehyde and syntans have been carried out. Such combination tannages would also lead to an increase in hydrothermal stability of the leathers.[8] Sodium metasilicate, is known to give fuller white leathers with light fastness, suppleness and good feel.[9] Hence, use of silica as a co-tanning agent is expected to improve the properties of zirconium oxychloride leathers. Glutaraldehyde finds an important application in combination tanning for the production of garment leathers where soft and full perspiration resistant leather is desired.[10] Post tanning methods also needs to be optimized to produce both upper and garment leathers to prove the versatility of zirconium oxychloride-citrate tanning system.

EXPERIMENTAL

Raw material

Wet salted goat skins of weight range 1-1.5 Kg were

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processed up to pickling using conventional recipe. Three pickled skins were used for each tanning trial.

Pretreatment with Syntan

Pretreatment with syntan could lead to the improvement in grain characteristics of the leathers when treated with zirconium salts11. Hence pickled goatskins in the weight range of 1 Kg were pretreated with two types of syntans followed by the tanning with zirconium oxychloride - citric acid. The two syntans selected for pretreatment are:

1. **Syntan A**: Napthalene-sulphonic acid and urea-formaldehyde condensate[12]
2. **Syntan B**: Polymeric syntan based on multifunctional polycarboxylic acid and sulphonated aromatic hydrocarbon[13]

Optimization of Syntan

Pickled goatskins were pre treated with the syntans A and B (1, 2 and 3%) followed by zirconium tanning in the same bath. By varying the % of syntan offered the amount of syntan used for pretanning was optimized based on the hydrothermal stability and grain characteristics of the resulting leather.

Syntan A/B	:	X % run for 30 min. X = 1,2,3
$ZrOCl_2$ + Citric acid	:	2 % as ZrO_2 3 feeds@ 10 min interval and finally run for 60 min.
Water	:	50% run for 30 min & basified to pH 3.8-4.0

Studies on Combination Tannages

In order to improve the properties of leathers, studies on combination tannage of zirconium oxychloride with sodium metasilicate and gluteraldehyde has been carried out.

Optimization of Sodium Metasilicate

In zirconium oxychloride - silica combination tannage, the amount of silica has been optimized. Sodium metasilicate of varying amounts (1, 2 and 3%) was used for the optimization experiments. The pickled pelt was treated with zirconium oxychloride-citric acid followed by sodium metasilicate. Leathers were evaluated for hydrothermal stability and grain characteristics and the % offer was optimized.

Optimization of Gluteraldehyde Syntan

In zirconium oxychloride - glutaraldehyde tannage, the skins were pretreated with varying percentages (1, 2 and 3 %) of gluteraldehyde syntan (Relugan GT 50)[14] followed by zirconium oxychloride-citric acid. The % offer was optimized based on the hydrothermal stability and grain characteristics of the leathers obtained.

Tanning Trials

Different tanning trials with zirconium oxychloride were carried out in order to improve the hydrothermal stability and other organoleptic properties of final leathers. Tanning trial experiments using pickled goatskins were carried out with the optimized amount of co-tanning agents along with zirconium oxychloride and citric acid system6. The tanning trial of zirconium oxychloride without any tanning adjuncts (control I) and conventional chrome tanning trial (control II) using pickled goatskins were also carried out. The hydrothermal stability and the exhaustion of zirconium were analyzed for all the tanning trials.

Various tanning experiments employed were as follows

Expt. I - Syntan A + ($ZrOCl_2$ + citric acid)
Expt. II - Syntan B + ($ZrOCl_2$ + citric acid)
Expt. III - ($ZrOCl_2$+ citric acid) + Sodium metasilicate
Expt. IV - Glutarldehyde syntan (GT50) + ($ZrOCl_2$ + citric acid)
Control I - ($ZrOCl_2$ + citric acid)
Control II - Conventional chrome tanning

Similar set of tanning trials were also carried out using pickled sheep skins.

Standardization of Neutralization Process for Post Tanning

Leathers from goatskins tanned with zirconium oxychloride-citrate system were post tanned with and without neutralization. The post tanning without neutralization was carried out as mentioned in Table I. In the case of post tanning with neutralization, the zirconium oxychloride treated leathers were neutralized to a pH of 5.5 and post tanned using the recipe mentioned in Table I. The leathers post tanned with and without neutralization were analyzed for their organoleptic properties.

Post Tanning Process

Leathers obtained from different tanning trials were subjected to post tanning. Leathers from goatskins were shaved to a uniform thickness of 1.2 mm and post tanned into white upper crust leathers as mentioned in Table I. Leathers from sheepskins were shaved to a uniform thickness of 0.8mm and post tanned to obtain white garment crust leathers using the recipe described in Table II. The crust leathers were analyzed for their physical strength and organoleptic characteristics.

Estimation of Zirconium[15]

The spent tan liquors from the tanning trials of experiments and control I were collected and the zirconium content in the liquors were analyzed as per the procedure given below.

TABLE I
Post Tanning Methodology for Upper Leather
(% offer based on shaved weight)

Operation	Chemicals	% (based on shaved weight)	Time (min.)	Remarks
Washing	Water	200	10	Drain
Retanning & Fatliquoring	Water	100		
	Acrylic syntan[1]	2	30	
	Protein syntan[2]	2	30	
	Resin syntan[3]	3	30	
	Replacement syntan[4]	3		
	White syntan[5]	3	60	
	Synthetic fatliquor[6]	2		
	Vegetable fatliquor[7]	2	30	
	Synthetic fatliquor[6]	3		
	Semisyn. Fatliquor[8]	2	60	
Fixing	Formic acid	2	3x10+30	Check exhaustion, Drain
Top Fatliquoring	Water	100		
	Cationic fatliquor[9]	0.5	20	Drain, piled
Set, hooked to dry, staked & buffed				Next day

1. Acyrlic syntan: Relugan RE (BASF Ltd)
2. Protein syntan: Sellasol PR (TFL)
3. Resin syntan: Basyntan FB6 (BASF Ltd), Tergotan GSI (Clariant)
4. Replacement syntan: Basyntan AN (BASF Ltd)
5. White syntan: Basyntan DLE (BASF Ltd)
6. Synthetic fatliquors: Cutapol WK (Dr.Th. Bohme), Lipoderm Liquor SA (BASF Ltd), Sandolix WWLI and Dermalix CFL (Clariant),Balmol SXE (Balmer Lawrie)
7. Vegetable based fatliquor: Dermalix GRC (Clariant)
8. Semi-synthetic fatliquor: Dermalix MKG (Clariant)
9. Cationic fatliquor: Catalix GSIN (Clariant)

Reagents: The reagents used were of analytical grade, which includes acid mixture (perchloric-, nitric- and sulphuric acid mixture in the ratio 11.5:5.0:3.5), 10% solution of hydrofluoric acid, ammonium chloride, ammonium tartrate, ammonia, 8-hydroxyquinoline (5%) in acetone, chloroform and anhydrous sodium sulphate.

Procedure: An aliquot (10 ml) from the spent liquor was digested using 20ml acid mixture. The solution was cooled and made up to known volume. An aliquot containing 20 - 200 mg zirconium was transferred to a 150 ml beaker. Dilute hydrofluoric acid (10 ml of dilute 48% hydrofluoric acid 1:10) and ammonium chloride - ammonium tartrate solution (10 ml prepared by dissolving 120 g of ammonium chloride and 120 g of ammonium tartrate in 1 liter of water at 25°C) was added. The solution was made nearly neutral with ammonia and diluted to 50 ml with water. The pH was adjusted to 8.9 ± 0.1 with ammonia. Solution of 8-hydroxyquinoline (5%) in acetone (1 ml) was added and allowed to stand for 30 min. Then the solution was transferred to a 125 ml separating funnel and extracted with three 10 ml portions of chloroform, shaking for 30 sec. each time. The extracted sample was taken in a 50 ml volumetric flask, and made up to the mark. Anhydrous sodium sulfate (1.0 g) was added to remove any trace of water. A blank was also carried out employing the same procedure without zirconium. The absorbance of the sample was measured at 386 nm using chloroform as reference. After suitable blank corrections of absorbance, the amount of zirconium in the sample was determined from a calibration curve prepared from standard zirconium solutions.

Determination of Shrinkage Temperature

The shrinkage temperature, which is a measure of hydrothermal stability of leather, was determined using a Theis shrinkage meter.[16] Each value reported is an average value of three samples.

TABLE II
Post tanning Methodology for Garment
(% offer based on shaved weight)

Operation	Chemicals	% (based on shaved weight)	Time (min.)	Remarks
Washing	Water	200	10	Drain
Retanning & Fatliquoring	Water	100		
	Resin syntan[3]	2	30	
	Protein syntan[2]	2	30	
	Synthetic fatliquor[6]	2	20	
	Resin syntan[3]	2		
	White syntan[5]	2	45	
	Synthetic fatliquor[6]	3		
	Semisyn. Fatliquor[8]	2	30	
	Synthetic fatliquor[6]	3	30	
	Lecithin fatliquor[10]	3		
	Fish oil fatliquor[11]	3		
	Dispersing agent[12]	0.5	60	
Fixing	Formic acid	2	3x10+30	Check exhaustion, Drain, pile
Set, hook to dry, staked & buffed				Next day

Superscripts 2 - 8, see Table I
10. Lecithin based fatliquor: Adumine EGG (Curtain SA)
11. Fish oil based fatliquor: Sulphirol C (Smit-zoon)
12. Dispersing agent: Tergolix AI (Clariant)

Physical Testing of Leather Samples
The samples for physical testing were obtained as per IULTCS methods.[17] The samples were conditioned at 80 ± 4 °F and 65 ± 2% R.H. for 48 hrs. Physical properties such as tensile strength, % elongation, tear strength, and grain crack strength were investigated. Each value reported is an average value of four samples.

Evaluation of Organoleptic Properties
Upper crust leathers were assessed for grain smoothness, grain tightness, fullness and general appearance. Garment leathers were assessed for softness, grain smoothness and general appearance. Assessments were made by standard tactile evaluation technique. Experienced tanners rated the leathers on a scale of 0-10 points for each functional property.

Results And Discussion

Optimization of Syntan
Zirconium tanned leathers, in general exhibit drawn grain characteristics. Drawn grain arises due to the astringency of the zirconium salts, which makes it highly reactive towards the pelts.[11] Pretreatment of pelts with syntan before treatment with zirconium oxychloride would reduce the reactivity of the pelt, hence reducing the drawn grain of the pelts. The approach is similar to the one that has been followed in the case of vegetable tanning system, wherein the pelts are pretreated with a low molecular weight phenolic syntan, so that the reactivity of the pelts towards vegetable tannins reduce. The properties exhibited by zirconium oxychloride tanned leathers pretreated with two different syntans at different amount are shown in Table III. The grain characteristics of the leathers have been found to be improved by the pretreatment with syntans, especially pretreatment with 2 and 3% syntan B, which is based on multi-functional polymer and produced better leathers with respect to the grain characteristics. The hydrothermal stability of zirconium oxychloride tanned leathers pretreated with these syntans is also presented in the table. There is a slight increase in hydrothermal stability of leather, which has been pretreated with syntans, when compared to leathers treated only with citric acid masked zirconium oxychloride, which exhibited a shrinkage temperature of 94°C. Zirconium oxychloride - citrate tanned leathers pretreated with 2% syntan A, which is based on naphthalene sulphonic acid - urea formaldehyde condensate exhibited shrinkage temperature of 97°C, which is 2°C greater than those pretreated with 1% of the same syntan. Whereas, syntan B produces leathers of shrinkage temperature 95°C at 2% offer and the shrinkage temperature remained the same when the syntan offer increased to

TABLE III
Hydrothermal Stability and Visual Assessment Data of the Zirconium Oxychloride (with citric acid) Tanned Leathers Pretreated with Syntans

Syntans	% offer based on pelt weight	Shrinkage temperature (T_s °C) ± 1	Visual assessment of grain characteristics (0-10 scale)
Syntan A	1	95	6
	2	97	7
	3	97	7
Syntan B	1	94	7
	2	95	8
	3	95	8
Control I	-	94	6

TABLE IV
Hydrothermal Stability of Leather Tanned with Masked Zirconium Oxychloride in Combination with Sodium Metasilicate and Gluteraldehyde

Co-tanning adjuncts	% offer based on pelt weight	Shrinkage Temperature (T_s °C) ± 1
Sod silicate	1	94
(Post-treatment)	2	93
	3	92
Gluteraldehyde Syntan	1	96
(Pre-treatment)	2	97
	3	99

3%. Hence, 2% pretreatment of syntans has been optimized for experimental tanning trials.

Optimization of Sodium Metasilicate and Gluteraldehyde Syntan
The primary objective of the present work is to develop zirconium oxychloride tanning system which can be used to produce leathers with good properties and for different product mix. Sodium metasilicate and glutaraldehyde have been chosen to act as tanning adjuncts to improve the properties of leathers tanned with zirconium oxychloride. The hydrothermal stability of leathers obtained from the combination tanning system is shown in Table IV. It has been reported that silica pretreatment hinders zirconium tannage, whereas silica post-treatment does not hinder zirconium tannage,[18,19] hence sodium metasilicate treatment is carried after the treatment of zirconium oxychloride - citric acid. Combination of zirconium oxychloride re-treated with 1 % sodium metasilicate produced leathers with shrinkage temperature of 94°C. The hydrothermal stability is found to decrease when the amount of sodium metasilicate is increased from 1 to 3 %. On the other hand, pretreatment of gluteraldehyde increases the hydrothermal stability of the zirconium oxychloride tanned leather. The shrinkage temperature of 1% gluteraldehyde pretreated leathers was found to be 96°C, which increased to 99°C when 3% gluteraldehyde was used. But the leathers post-treated with 3% sodium metasilicate produced fuller leathers compared to other treatments. Hence, experiments involving post-treatment with 3% sodium metasilicate and pretreatment with 3% gluteraldehyde have been optimized for the tanning experiments.

Tanning Trials
The hydrothermal stability and the exhaustion details of the experimental and control tanning trials is presented in Table V. The leather tanned with zirconium oxychloride in the presence of 0.3 moles of citric acid has been used as the control leathers (control I) to compare the influence of other tanning adjuncts on the properties of the leather. Except for the leathers pretreated with gluteraldehyde (3%), which exhibit Ts of 99°C, there is not much change in hydrothermal stability of leathers from the other experiments compared to control I. Chrome tanned control leathers (control II) exhibited a shrinkage temperature of 110°C. It is seen from Table V that there is no significant change in the exhaustion of zirconium for different experiments and the value remains greater than 80% for all the experiments including control.

Standardization of Neutralization for Post Tanning
When a conventional way of post tanning method was

TABLE V
Exhaustion and Shrinkage Temperature of Experimental and Control Leathers

Expt.	Experimental details	% Uptake of zirconium	Shrinkage temperature (T_s °C) ± 1
C I	$ZrOCl_2$ + citric acid	81 ± 1	94
C II	Basic chromium sulphate	-	110
E I	Syntan A + ($ZrOCl_2$ +citric acid)	83 ± 2	97
E II	Syntan B + ($ZrOCl_2$ +citric acid)	83 ± 1	95
E III	($ZrOCl_2$ +citric acid) + Sodium metasilicate	85 ± 2	92
E IV	Gluteraldehyde + ($ZrOCl_2$ +citric acid)	83 ± 1	99

TABLE VI
Visual Assessment of Zirconium Oxychloride-Citric Acid Tanned Leathers Post Tanned with and without Neutralization

Organoleptic characteristics	With neutralization	Without neutralization
Softness	4	6
Fullness	6	7
Grain tightness	5	6
Grain Smoothness	5	6
General Appearance	5	7

* Scale 0 represents poor and 10 represents very good

TABLE VII
Strength Characteristics of Upper Leathers Made from Different Experiments and Controls

Experiments	Tensile strength (Kg/cm^2)	% Elongation	Tear strength (Kg/cm)	Load @ Grain crack (Kg) ± 2
C I	290 ± 11	48 ± 1	39 ± 2	31
C II	270 ± 10	60 ± 3	40 ± 3	33
E I	300 ± 15	52 ± 2	73 ± 4	43
E II	325 ± 12	50 ± 2	52 ± 3	45
E III	335 ± 14	48 ± 3	75 ± 6	41
E IV	252 ± 9	47 ± 1	43 ± 2	41

employed, the leathers exhibited poor uptake of post tanning auxiliaries. This necessitated a look at the method of post tanning that was adopted. Also an understanding of the mode of binding of zirconium salts becomes necessary. Earlier studies on the mechanism of interaction of zirconium salts with collagen indicated that zirconium complexes bind with amino groups of collagen.[8,20] Later studies showed that both amino as well as carboxylic groups are involved in the binding of zirconium salts with collagen and physical deposition had also been shown to take place.[21,22] In the present tanning study, masked zirconium oxychloride is used for tanning. If zirconium oxychloride interacts with both amino and carboxylic group, the anionic auxiliaries added during post tanning would have fewer sites for binding with collagen matrix except for the residual charges present on the zirconium complexes, which are bound to the collagen. If the residual charges present in the zirconium-tanned leather are neutralized, then there may not be any site for binding of the fatliquors and other auxiliaries. Also there are reports available about the shift in the iso-electric point towards lower pH for the leathers treated with zirconium salts. Therefore, experiments have been carried in order to monitor the influence of neutralization. Masked (using 0.3 moles of citric acid) zirconium oxychloride leathers have been post tanned with and without neutralization and the organoleptic properties analyzed are shown in Table VI. From the table it is clear that all the organoleptic properties of the crust leathers are found to improve when neutralization is avoided. The exhaustion of the spent liquor is also found to improve when post tanning is carried out without neutralization.

Upper Leathers from Zirconium Oxychloride Tanning

The experimental and control leathers tanned from

TABLE VIII
Strength Characteristics of Garment Leathers Made from Different Experiments and Controls

Experiments	Tensile strength (Kg/cm^2)	% Elongation	Tear strength (Kg/cm)	Load @ Grain crack (Kg) ± 2
C I	205±9	66±2	50±3	30
C II	165±6	71±3	37±2	32
E I	216±10	70±2	53±4	36
E II	225±7	72±2	54±4	33
E III	232±9	71±2	55±5	35
E IV	163±5	61±2	38±1	35

goatskins have been post tanned for upper leathers. The strength characteristics of upper leathers from different tanning trials are shown in Table VII. Upper leathers made from combination system of zirconium oxychloride and silica, E III exhibit higher tensile strength of 335 Kg/cm^2, compared to other experiments and control. They also exhibit higher tear strength (around 75 Kg/cm). Zirconium oxychloride leathers pretreated with gluteraldehyde exhibit lower strength characteristics compared to other experimental and control leathers. Grain crack strength is also found to be more than 40 Kg for all experimental leathers except control, which exhibits resistance to crack until 31 Kg. All the strength properties of the experimental and control leathers are higher than the standard values for upper leather.[23] Visual assessment of the upper leathers is shown in Figure 1. The masked zirconium oxychloride tanned leather, pretreated with 2% gluteraldehyde (E IV), shows good grain smoothness, however, the experiment E III shows better grain tightness and overall appearance for the upper leather compared to other experimental and control leathers.

Garment Leathers from Zirconium Oxychloride Tanning

A set of experimental and control leathers made from sheep skin using the tanning trials has been post tanned for garment leathers. The visual assessment results of the leathers are shown in Figure 2. From the figure it is clear that gluteraldehyde pretreatment (E IV) resulted in soft and smooth leathers. These leathers have been found to be better in all the properties compared to other experimental and control leathers. The strength properties of the garment leathers are shown in Table VIII. It is interesting to note that the trend on the strength properties of various experimental leathers is similar to those obtained for leathers from goatskin. Leathers from E IV i.e pretreated with gluteraldehyde showed lower tensile and tear strength properties compared to other experimental leathers. But the strength properties of E IV has been found to be similar to the strength exhibited by chrome tanned leathers (Control II), which produced leathers with tensile strength of 163 Kg/Cm^2 and tear strength of 38 Kg/Cm. However, E IV showed higher resistance to grain crack, 35 Kg. Leathers from other experiments and control I exhibited tensile strength above 200 Kg/Cm^2 and tear strength greater than 50 Kg/Cm. All the experimental and control leathers exhibited grain crack resistance above 30 Kg. Leathers tanned with zirconium

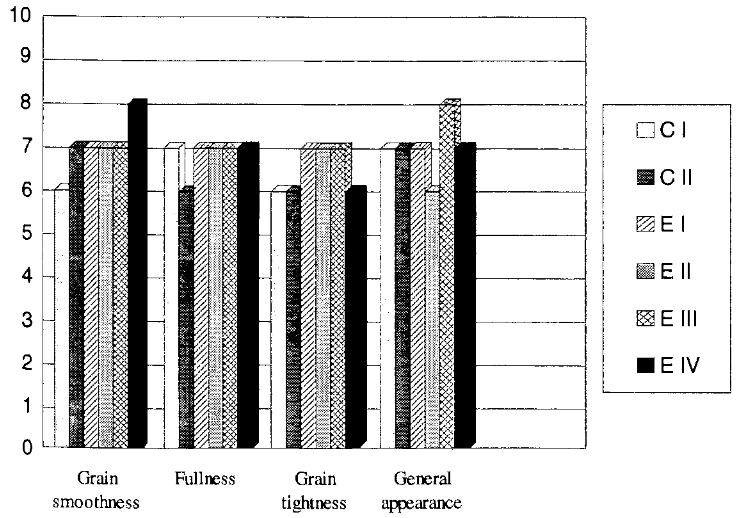

Figure 1. - Visual assessment of upper leathers made from different experiments and controls

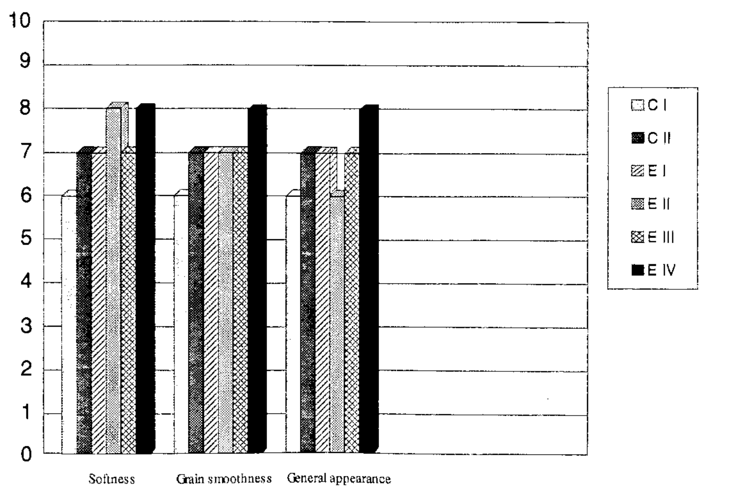

Figure 2. - Visual assessment of garment leathers made from different experiments and controls

salts have generally been used for producing firm leathers. In the present study, soft garment leathers have also been obtained by tanning with zirconium oxychloride system. Hence, its viability as an effective tanning system for producing leather for different end uses similar to the chrome tanning system has been established.

CONCLUSIONS

Tanning with zirconium oxychloride is an eco-friendlier alternative for chromium. The present study insinuates that there is a good potential for zirconium oxychloride tanning to evolve into a versatile tanning system. The major advantage of the tanning system using zirconium salts is the ability to produce white leathers, which is difficult in the case of other dominant tanning system existing at present. Both chromium and vegetable tanning systems induce a base color to the leathers, which leads to difficulty in producing pastel shades. Through the addition of suitable adjuncts and by the intervention of proper process control, leathers with good characteristics are obtained from the zirconium oxychloride tanning system. Zirconium oxychloride tanned leathers, post tanned for making upper, produced fuller and tighter leathers that are better than the chrome tanned leathers. Good soft leathers are obtained when the zirconium oxychloride leathers are post tanned for making garment leathers; especially gluteraldehyde pretreatment produced softer leathers. The strength properties of the zirconium oxychloride tanned leathers have been found to be good when compared to chrome tanned leather. Thus, the zirconium oxychloride tanning system developed has the potential to be an alternative for the chrome tanning system.

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