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THE APPLICATION OF DIFFERENT DELIMING AGENTS FOR DECREASING AMMONIUM POLLUTION LOAD CAUSED BY DELIMING OPERATION IN LEATHER INDUSTRY AND THE EFFECTS OF THESE DELIMING AGENTS ON LEATHER QUALITY AND EFFLUENT POLLUTION LOAD

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ABSTRACT

Effluent which has a high content of ammonium load is produced as a result of traditional deliming operation during the leather production. In this operation, ammonium salts are being used. Among the production processes the highest rate of ammonium content is originated from the traditional deliming operation. The NH_3 in water is a source of pollution. Ammonia is converted into nitrate by means of nitrogen cycle in nature. The ammonium discharged into natural water sources has toxic effects on living organisms.

In this research by application of weak acids studies on sheep skins were made to reduce the ammonium load that originated from deliming operation. Beside the deliming effect of acids, N content of the resulting discharge water was determined and the effect of these methods on the quality of the leather was studied. The data obtained from the study were compared with the traditional deliming methods and standards.

Key Words: leather, deliming, weak acid, ammonium salts, environment

ÖZET

Deri üretimi sırasında geleneksel kireç giderme işlemi sonucunda amonyum içeriği yüksek atık sular ortaya çıkar. Bu yöntemde genellikle amonyum tuzları

kullanılmaktadır. Üretim prosesleri sırasında en yüksek amonyum içeriği geleneksel kireç giderme işleminden kaynaklanmaktadır. Sulardaki NH_3 konsantrasyonları önemli bir kirlilik kaynağıdır. Amonyak doğadaki azot çevriminde nitrata dönüşür. Doğal sulara deşarj edilen amonyum canlılar için zehir etkisine sahiptir. Araştırmada, kireç giderme işleminden kaynaklanan amonyum yükünü azaltmak için farklı asitler kullanılarak çalışmalar yapılmıştır. Çalışmada asitlerin kireç giderici etkisinin yanında, işlem sonucu ortaya çıkan atık suların N içerikleri tespit edilmiş ve bu yöntemlerin derilerin kalitesi üzerine etkisi araştırılmıştır. Çalışmada elde edilen veriler, geleneksel kireç giderme yöntemleriyle ve standartlarla karşılaştırılmıştır.

Anahtar Kelimeler: deri, kireç giderme, zayıf asit, amonyum tuzları, çevre

1. INTRODUCTION

In leather production the process of liming, is performed for removing the epidermal structure, opening up fibrillar structure by swelling, and forming active carboxyl and amino groups with which chemicals given in tanning and following processes, can bond to leather. During liming process pH of leather is raised to 12-13. At the end of this process pH value of leathers have to be reduced by deliming process to a pH level at which bating process can be performed. Ammonium salts are commonly used in deliming processes around the world.

Ammonium salts are the most commonly used deliming agents because they quickly penetrate into the hide and have a buffering action regulates the pH at optimal values and penetrating quickly[5]. In recent years due to environmental problems limitation of ammonium salts used in deliming process is required[3]. The ammonium ions contained in tannery effluent are mainly generated at the deliming and bating stages. It is often very difficult and expensive to remove them in effluent treatment plants[16].

Up to 70% of the ammonia ions discharged in tannery effluent is the result of the use of ammonium sulfate in the deliming and bating preparations[6]. The ammonium loads discharged in effluents from individual leather processing operations are presented in Figure 1[7].

The reduction of ammonium load in leather industry effluents is environmentally important. Beside being expensive and time-consuming the treatment of these effluents is toxic and hazardous for environment. The deliming phase using ammonium salts bring about considerable nitrogen pollution, estimated to be as much as 40% of total discharge[1]. The 13.5% of ammonium sulphate used in conventional deliming process is discharged into

effluent in the form of ammonia nitrogen and 13.5% is emitted into air as ammonia gas. This gas is toxic and may pose risk for the health and safety of workers[15].

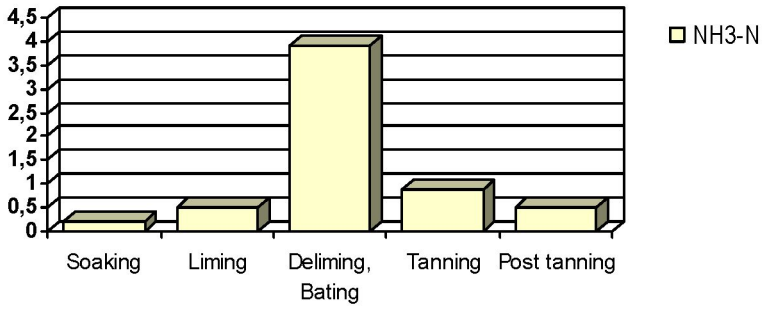

Figure 1: Discharged ammonium load from individual leather processing operations

Nitrification caused by high ammonium content increases biological oxygen demand of effluents. Leaking of these effluents into the streams may cause fish and other aquatic living organism to die.

Boric acid, magnesium lactate, organic acids such as lactic acid, formic acid and acetic acid or esters of organic acids can be used to substitute ammonium salts. When used in deliming process weak acids provide some advantages. The most important one is they penetrate easily and fast into the skin owing to having non-swelling effect. Positive effects on the quality of the pelts are observed when used in deliming process[4]. In this study various weak acids and conventional deliming agent ammonium sulphate was used. The nitrogen content of effluents from deliming process was determined. The quality of the pelts processed according to these methods was determined by chemical and physical tests. The values obtained were compared with standards and leathers produced by conventional deliming process.

2. MATERIAL AND METHOD

MATERIAL

The study was conducted on salt-dried domestic sheep skins and the number of skins used was 3. Deliming processes of skins were carried out by using four different deliming agents like acetic acid (99.8%, technical grade), boric acid (99.5%, analytical grade), citric acid (99.5%, analytical grade) and ammonium sulphate. All experiments were done in triplet and laboratory-scale drums were used.

METHOD

Following soaking, unhairing and liming processes sheep skins were split into four pieces of equal size and each piece was delimed with a different deliming agent. The pH of deliming float was determined as 13.0. Deliming procedure is presented in Table 1.

Table 1: Deliming procedure recipe

Deliming procedure recipe					
Process	**%**	**Product**	**Temperature(^{0}C)**	**Time (min)**	**pH**
WASH (x2)	100	Water	35	10	-
DRAIN					
DELIMING *(In different drums)*	100	Water	35		
	1.5	**Acetic acid**		30	~ 8.0
	100	Water	35		
	3.5	**Boric acid**		30	~ 8.0
	100	Water	35		
	2	**Citric acid**		30	~ 8.0
	100	Water	35		
	2	**Ammonium Sulphate**		30	~ 8.0

*Percentages are based on the weight of leather sample

Afterwards samples were taken from the deliming float and total nitrogen (N) content of effluents were measured photometrically by using test kits and Merck SQ 300 device.

Skins were processed into leathers according to the following recipe (Table 2) after the deliming and bating processes.

Table 2: The recipe of degreasing, pickling, tanning, neutralisation and dyeing procedures

Degreasing, pickling, tanning, neutralisation and dyeing procedures					
Process	%	Product	Temperature (^{0}C)	Time (min)	pH
DEGREASING	4	Gemdegriz Deritoff 100®		60	
WASHING	150	Water		10	
DRAIN					
	150	5Be´ Salty water		15	
DRAIN					
	150	5Be´ Salty water		20	
DRAIN					
PICKLING	100	7Be´ Salty water	35	10	
	1	Formic acid (3x10)		30	
	0.5	Sulphuric acid (2x15)		30	~ 3.0
TANNING	4	Tankrom SB® (2x45´)		90	
	0.6	Coratyl OL®		6 hr, overnight 15 min/hour	~ 0.5
	0.5	Sodium bicarbonate (3x5´)		15	~ 4.0

NEUTRALISATION	150	Water	35		
	3	Tankrom SB®		40	
	1	Sodium formate		20	
	1	Sodium bicarbonate (1:20) (1x3)		45	~ 5.0
DYEING	60	Water	35		
	3	DRASİL TX®		15	
	3	Vandotan AZ®		15	
	2	Pellutax 385®		15	
	3	Dye		45	
	200	Water	70		
	5	SANDOLIX WWL®			
	2	GRASSAN PA®			
	2	PELLASAN MOL®		60	
	1.5	Formic acid (1:10) (1x3)			~ 3.8
DRAIN					
WASHING					
DRYING					

In order to determine the quality and physical resistance parameters of leathers processed by these methods tests like tensile strength, elongation at break and tear strength were made according to TS.4119[11], TS.4118[10] standards of Turkish Standards Institution.

Analysis for determination of chromic oxide, sulphated total ash and sulphated water-insoluble ash and matter soluble in dichloromethane in leather were made in accordance with TS.4126[14], TS.4125[13] and TS.4124[12] standards. Calcium determination was done with calcium filter and acetylene/air mixture using Eppendorf Gerätebau Flame Photometry. Each leather sample was tested in accordance with standard methods in triplets.

3. RESULTS AND CONCLUSION

Nitrogen is found in effluents in the form of ammonia nitrogen, nitrate nitrogen, nitrite nitrogen and organic nitrogen. It is a criterion that must be measured in surface water and contaminated water. The nitrogen content originated from structure of leather and ammonium sulphate used in conventional deliming process is the main source of nitrogen in deliming effluents. Total nitrogen values obtained from the measurement of the effluent samples taken from deliming float were given in Figure 2.

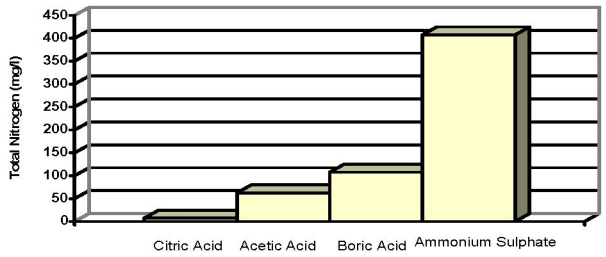

Figure 2: Total Nitrogen Values of Deliming Effluents

It is reported that the nitrogen content of leather industry effluents discharged directly into the surface water is must be between 3-10 mg/l[9]. Industrial ammonia nitrogen level of leather industry is given as 83-159 mg/l[8].

As can be seen in Table 3, total nitrogen values are seemed to vary between 17 mg/l and 350 mg/l. According to these values the deliming agent which has the lowest total nitrogen value is citric acid and acetic acid and boric acid has higher values respectively.

Table 3: Total Nitrogen Values of Deliming Effluents

Deliming Agents	**Total N (mg/l)**
Citric Acid	17
Acetic Acid	60
Boric Acid	80
Ammonium Sulphate	350

The highest total nitrogen value among the deliming agents was measured for ammonium sulphate. Though the total nitrogen values of citric acid, acetic acid and boric acid were below the discharge limits, the value of ammonium sulphate is reasonably above the limits.

Table 4: Chemical Analysis Results of Leathers Processed Using Different Deliming Methods

Deliming Agents	**Cr_2O_3 %**	**Fat and Oil %**	**Ash %**	**Calcium %**
Acetic Acid	3.75	5.1	2.69	0.2530
Boric Acid	3.79	6.1	2.38	0.2532
Citric Acid	3.77	5.2	2.47	0.2523
Ammonium Sulphate	3.76	11.9	2.43	0.2559
UNIDO[8]	min. 2.5	4-10 %	max. 2	-

The chemical analysis results of leather samples were given in Table 4 and Figure 3, 4, 5.

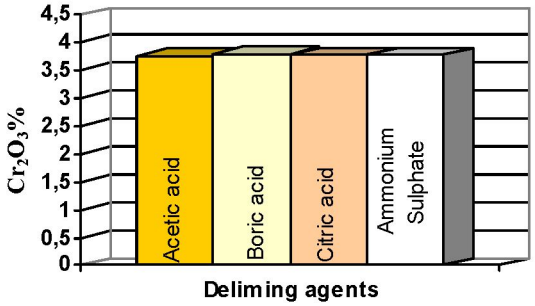

Figure 3: Cr_2O_3 % Content of Leather Samples

There doesn't seem to be significant differences in terms of chromic oxide content of leather samples but the highest value was measured for the leather delimed with *boric acid* (Figure 3). All leather samples provided values above the 2.5% chromic oxide content sub-limit of acceptable quality levels in leathers that indicated by United Nations Industrial Development Organization, UNIDO[2]. Although all processes except deliming-bating were done in the same float fat and oil analysis results of acetic acid, boric acid, and citric acid are close to each other, the value for ammonium sulphate is slightly above 10% the top-limit of UNIDO[2] (Figure 4). It's thought to be due to taking samples

from different sides of the skin. Because of being a natural material, considerable variation of physical and chemical structure is found in different sides of animal skins.

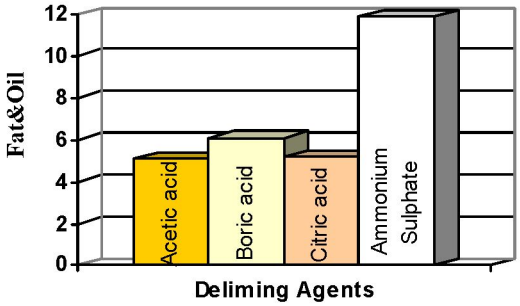

Figure 4: Fat&Oil % Content of Leather Samples

As the ash contents of leather samples were examined boric acid delimed leather samples provided the minimum ash% content. Ammonium sulphate and citric acid delimed leathers provided higher ash% contents respectively and acetic acid delimed leather the highest (Figure 5). According to calcium measurements by using Flame Photometry, all values were found to be close to each other and ammonium sulphate delimed leather showed the maximum value.

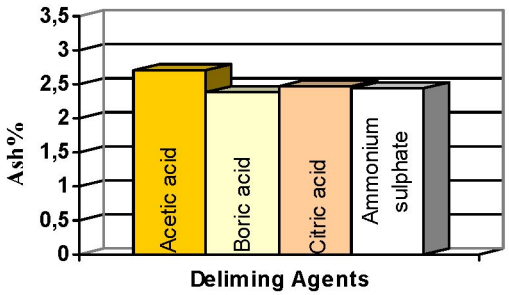

Figure 5: Ash% content of leather samples

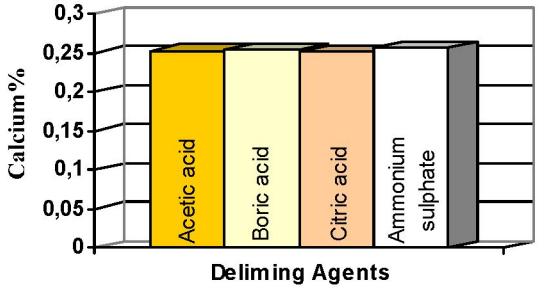

Figure 6: Calcium% content of leather samples

Table 5: Physical Test Results of Leathers Processed Using Different Deliming Methods

Deliming Agents	Tensile strength (daN/cm^2)	Elongation at Break (%)	Tear strength (N/cm)
Acetic Acid	119.4	77.5	37.5
Boric Acid	133.6	73.5	38.8
Citric Acid	166.7	75.8	39.8
Ammonium Sulphate	127.9	89.0	37.8
UNIDO[2]	min. 100	max. 60	min. 15

The data obtained from tensile strength, elongation at break and tear strength test which were done in addition to chemical analysis to compare the qualities of leathers, are presented in Figure 7, 8, 9 and Table 5.

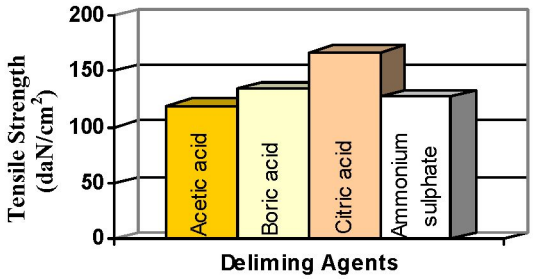

Figure 7: Tensile Strength of Leather Samples

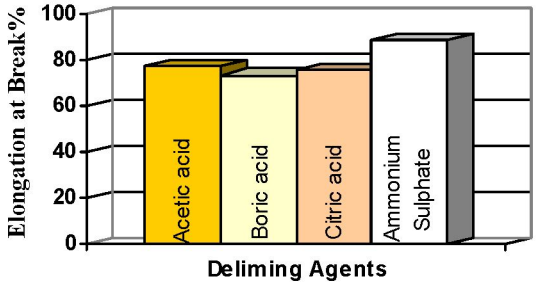

Figure 8: %Elongation at Break of Leather Samples

The tensile strength values of leather samples were quite above the acceptable 100 (daN/cm^2) sub-limit value. The highest tensile strength value was observed with citric acid delimed leather. It is thought to be due to the formation of two different buffer systems that prevent unexpected pH changes, so less damage is given to fibers (Figure 7).

Owing to skin structure, the values obtained for elongation at break tests were found to be higher than the elongation top-limit of 60% that indicated by UNIDO[2] (Figure 8).

Tear strength values obtained were quite above the 15 (N/cm) sub-limit. Citric acid delimed samples provided the highest tear strength values (Figure 9). Boric acid showed lower tear strength value than citric acid samples and acetic acid samples showed the lowest value (Table 5).

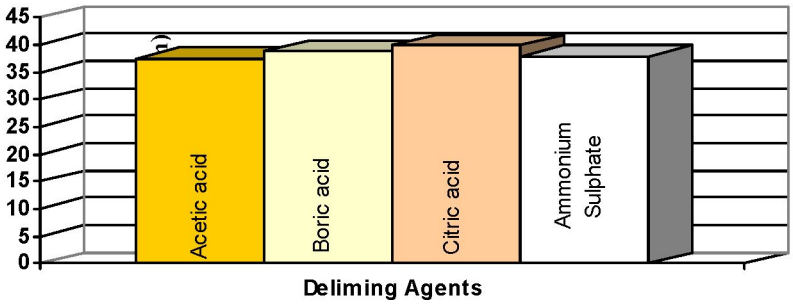

Figure 9: Tear strength values of leather samples

The leather quality specifications obtained by using different acids and ammonium sulphate in deliming process were found to be close to each other.

When nitrogen content sourced by deliming process was examined it was determined that acid delimed samples contained quite less concentrations of nitrogen and especially effluent of citric acid delimed samples had the minimum nitrogen content among other acids.

According to data obtained from this study using acids for decreasing pollution caused by ammonium salts may be suggested.

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