(REFEREED RESEARCH)

USAGE OF HYDROGEN PEROXIDE IN LEATHER MANUFACTURING PROCESSES AND ITS EFFECTS ON LEATHER CHARACTERISTICS

HİDROJEN PEROKSİDİN DERİ İŞLEM BASAMAKLARINDA KULLANIMI VE DERİ ÖZELLİKLERİNE ETKİSİ

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ABSTRACT

In this study, hydrogen peroxide usage instead of sodium sulphide (Na_2S) under alkaline condition in leather manufacturing was investigated, whether hydrogen peroxide could be an alternative to high pollutant conventional unhairing-liming process or not. Besides, the effect of hydrogen peroxide on leather properties and the pollution load of liming wastewater were studied. The results indicated that the unhairing and fiber opening performance of hydrogen peroxide were satisfactory and the physical characteristics of the leathers as well as the air permeability values were comparable to those obtained by conventional unhairing-liming process. In addition, the chemical oxygen demand (COD) and the sulfide values of the waste water were also lower than the conventional one.

Key Words: Hydrogen peroxide, Sodium hydroxide, Liming, Enzymatic bating process.

ÖZET

Bu çalışmada; deri işlem basamaklarında hidrojen peroksidin alkali ortamda Na_2S'ün yerine kullanılması ile yüksek oranda kirlilik yüküne sahip geleneksel kıl giderme-kireçlik işlem basamaklarının yanında enzimatik sama işleminede alternatif olup olmayacağı, mamul deri özellikleri üzerine etkisi ve atık sularındaki atık yükleri araştırılmıştır. Hidrojen peroksidin kıl giderme/kireçlik ile lif açılımı performansının yeterli olduğu, derilerin fiziksel özelliklerinin ve hava geçirgenliği değerlerinin geleneksel yöntemlerle işlenen deriler kadar iyi olduğu ve işlentiler sonunda atıksulardaki KOİ ve sülfit değerlerinin son derece düşük olduğu tespit edilmiştir.

Anahtar Kelimeler: Hidrojen peroksid, Sodyum hidroksid, Kireçlik, Enzimatik sama işlemi.

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1. INTRODUCTION

Worldwide concern over the environmental impact of leather industry has resulted in tanners coming under pressure to minimise elements of their effluents or to use environmentally friendly chemicals. It is well known that beamhouse operations especially liming process cause the highest pollution during the leather manufacturing processes (1-3). The main sources of ammonia are liming/unhairing processes and also deliming process in which mainly ammonium salts are used. It is known that the compounds including carbon disintegrated to CO_2, H_2O and the compounds including nitrogen disintegrated to NH_2 due to oxidation (4). Sulphide compounds like Na_2S are used with lime for liming/unhairing processes in conventional treatments. These compounds provide to swell the collagen fiber and skins and remove the wool from skin. Sulfide is very toxic and pollutant material for environment and it causes to hydrogen sulfide gas depending on pH value and oxygen consumption in medium (5,6). Due to this disadvantages, different chemicals and techniques are used as an alternative to the conventional unhairing process (7-10). One of these, which are based on the use of hydrogen peroxide under alkaline conditions, enables hair to be destroyed and removed from hide. The treatment of the residual effluent allows the protein to be precipitated and recovered. In this way, the polluting load in the effluent is reduced and the resulting water can be recycled in other operations (11). In this study by performing liming and enzymatic processes using hydrogen peroxide in alkali medium, it is aimed to find out how to affect leather characteristics and tannery effluent.

2. MATERIALS AND METHODS

For trials, same types of wet salted Irish sheepskins were used. Every skin was firstly divided into two pieces by backline and then each side of the leather was also divided into two equal pieces. By this way four pieces identical in characteristics were obtained.

In leather processing, standard chemicals used for leather manufacturing processes, were chosen. After soaking process, numbers were given to each sample and different pieces of the same skin were limed using different methods (Table 1, 2, 3). Liming process was carried out which are conventional liming with enzyme (CLB), conventional liming without enzyme (CL), liming with hydrogen peroxide with enzyme (LHPB) and liming with hydrogen peroxide without enzyme (LHP).

Table 1.Unhairing and enzymatic bating process performed to conventional treatment

Process	Substance	Temperature	Time
Unhairing	15 °Be Na_2S	25 °C	
	25 °Be $Ca(OH)_2$		4 hour
	200% Water	20 °C	
Liming	+2% Na_2S		
	+4% $Ca(OH)_2$		18 hour
Fleshing	calculated on	fleshed weight	
Deliming	100% Water	30°C	
	2% Organic acid mixture		30 min. pH 8,0
Bating	100% Water	37°C	
	+1% Enzyme preparate		40 min.
	Drum is drained		
Washing	200% Water	25°C	10 min.
	Drum is drained		

Table 2. Unhairing and enzymatic bating processes performed to H_2O_2 treatment

Process	Substance	Temperature	Time
Unhairing-Liming	100% Water	30 °C	
	2% NaOH		30 min.
	4% H_2O_2		2 hour
	Drum is drained		
Washing	200% water	25 °C	15 min.
	Drum is drained		
	x% Formic Acid(1:10)		pH 8,2
Bating	100% water	37 °C	
	+1% Enzyme preparate		40 min.
	Drum is drained		
Washing	200% Water	25 °C	10 min.
	Drum is drained		

Table 3. Subsequent processes treated to all samples

Process	Substance	Temperature	Time
Degreasing	100% Water	30 °C	
	5% Nonionic tenside		20 min.
	+100% Water	25 °C	30 min.
Washing	150% Water salt 4°Be	25 °C	30 min.
Pickle	100% Water, salt 7°Be	28 °C	
	1% Formic acid (1:10)		20 min.
	0,5% Sulphuric acid(1:15)		60 min. pH 3,0
Chromium Tanning	4% Chromium tanning agent		45 min.
	1% Basification agent		30 min.
	4% Chromium tanning agent		60 min.
	+1% Basification agent		6 hour pH 3,8

Sampling for Physical Tests and Chemical Analysis

Samples were conditioned for tests and analysis in accordance with TS EN ISO 2418 (12).

Tensile Strength and Elongation at Break, Hide Substance and Chromium Oxide

Leather samples taken in accordance with standard were cut into sizes indicated on TS 4119 EN ISO 3376 (13) using press machine. Hide substance of samples and chromium oxide analysis were done respectively in accordance with TS 4134 (14) and TS 4126 (15).

Air Permeability

Air permeability tests of leather samples were made with air permeability device. Samples were prepared in accordance with TS EN ISO 2419 (16) and were bonded with metal rings having different surface areas respectively 5cm^2, 20cm^2, 50 cm^2 and 200pA and 500pA pressure values were applied. At the end of the test period of two minutes, amount of air passed through leather was measured in m^3.

Scanning Electron Microscopy (SEM)

Samples taken before tanning process were fixed by glutaraldehyde and then fixation of lipids was performed with osmium tetroxide. Water content of samples was removed using different concentrations of ethyl alcohol respectively 30%, 50%, 70%, 85%, 95% and 100% (17,18). Next, hexamethyldisilazane was used for obtaining dried samples.

Chemical Oxygen Demand (COD)

After liming process there are high amounts of COD value in liming waste because of existing Na_2S and $Ca(OH)_2$ and substance based on keratin (19). With this parameter, oxygen demand required for chemical oxidation was indicated. For analysis, samples of liming wastewater belongs to trials were analyzed in accordance with TS 2789 ISO 6060 (20).

Sulfide Analysis

For sulfide analysis of liming wastewater, firstly, pH values of the wastewater samples were calibrated with sulphuric acid between pH 5 and 8. Then these samples were diluted with pure water and 3mL of it was added to standard sulfide test kit. Values obtained from spectrophotometer were multiplied with dilution ratio.

3. RESULTS AND DISCUSSIONS

Tensile Strength and Elongation at Break, Hide Substance and Chromium Oxide

As it can be seen from Table IV, hide substance ratio and the results showed that skin treated with conventional liming (CL) has lower chrome oxide content than conventional skin treated with conventional liming with bating (CLB). Bating process provides an increase in chromium oxide content of leather (21). The positive effect of bating process on chromium oxide uptake in hydrogen peroxide liming process is also can be seen. However, the important point is, because of appearing more carboxyl groups or anionic groups, the chromium oxide contents of hydrogen peroxide liming (LHP) and hydrogen peroxide liming with bating (LHPB) samples were found close to those conventionally processed leathers. Value of tensile strength and elongation at break ratio of the chrome tanned leather must be respectively at least 100 daN/cm^2 and 50% in accordance with UNIDO and it can be seen at Table 4 that all leather samples are higher than acceptable value (22).

Table 4. Results of some physical tests and chemical analysis belong to skin samples

Leather Sample	Tensile Strength (daN/cm^2)	Elongation at Break (%)	Hide Substance (%)	Chromium Oxide (%)
1.1CL	170,7	85	62.18	3,86
1.1CLB	157,3	80	61.58	4,22
2.1CL	180,6	92	63.44	4,01
2.1CLB	130,1	73	59.57	4,42
3.1CL	210,0	90	64.78	4,38
3.1CLB	186,8	75	63.98	4,62
4.1CL	147,0	82	65.64	4,02
4.1CLB	128,7	92	59.75	4,26
1.2LHP	180,5	98	57.83	3,98
1.2LHPB	140,4	93	55.08	4,33
2.2LHP	162,5	98	63.93	3,83
2.2LHPB	153,3	98	65.52	4,24
3.2LHP	146,5	98	65.49	4,30
3.2LHPB	135,4	66	63.40	4,61
4.2LHP	165,4	84	60.76	4,12
4.2LHPB	130,5	89	63.00	4,45

Table 5. The values of air permeability test for all applications (average thickness 1 mm)

Leather Sample No	2 min.					
	200 (Pa) Pressure			500 (Pa) Pressure		
	Surface Area			Surface Area		
	5 cm^2	20 cm^2	50 cm^2	5 cm^2	20 cm^2	50 cm^2
1.1CL	0,32	0,32	0,34	0,76	0,68	0,74
1.1CLB	0,37	0,27	0,56	0,70	0,56	1,22
2.1CL	0,22	0,23	0,23	0,48	0,48	0,49
2.1CLB	0,25	0,27	0,28	0,53	0,53	0,55
3.1CL	0,20	0,22	0,25	0,30	0,50	0,52
3.1CLB	0,24	0,35	0,44	0,33	0,64	0,65
4.1CL	0,32	0,34	0,35	0,74	0,78	0,46
4.1CLB	0,37	0,40	0,40	0,74	0,79	0,70
1.2LHP	0,13	0,13	0,13	0,30	0,36	0,31
1.2LHPB	0,30	0,81	0,75	0,60	0,64	0,58
2.2LHP	0,13	0,17	0,11	0,32	0,33	0,28
2.2LHPB	0,23	0,29	0,29	0,55	0,55	0,61
3.2LHP	0,21	0,21	0,21	0,46	0,44	0,43
3.2LHPB	0,26	0,20	0,20	0,40	0,40	0,38
4.2LHP	0,25	0,36	0,39	0,49	0,50	0,55
4.2LHPB	0,32	0,51	0,54	0,72	0,74	0,79

Air Permeability

The amount of air passed through conventionally unhaired, limed and unbated skin samples was found to be less than the bated skin samples (Table 5).

Likewise, samples, which bating process was applied, had higher air permeability values than unbated skins for hydrogen peroxide liming. This indicates that applied enzymatic processes, affected collagen fiber structure of skin and caused opening up of the fiber bundles and removed amorphous protein more effective found between fibrillary proteins. Variation of the values is thought to be due to regional differences of leather samples.

Chemical Oxygen Demand (COD) and Sulfide Analysis

It can be seen from Table 6 that COD results of the samples treated with hydrogen peroxide were found out lower than the conventional liming because of the chemicals breaking to CO_2 and H_2O.

Table 6. Result of the COD and sulfide measurements of waste of processes

	Leather Sample	COD (mgL^{-1})	Sulfide (mgL^{-1})
Conventional Liming	**1.1CL**	42300	2750
	1.1CLB	47900	3200
	2.1CL	43430	2950
	2.1CLB	47940	3180
	3.1CL	42600	2560
	3.1CLB	48000	2720
	4.1CL	43000	2890
	4.1CLB	49100	3340
Liming with Hydrogen Peroxide	**1.2LHP**	26540	50
	1.2LHPB	28350	56
	2.2LHP	27100	48
	2.2LHPB	28700	54
	3.2LHP	27500	52
	3.2LHPB	29000	57
	4.2LHP	25900	51
	4.2LHPB	27800	56

Scanning Electron Microscopy (SEM)

Bating process provides opening up of the fiber structure, which will done after conventional unhairing and liming processes (Figure 1, 2). If the SEM micrographs belongs to all samples are compared, it can be seen that opening up of the fiber structure of skins samples, which were treated with hydrogen peroxide and hydrogen peroxide with bated, are similar to conventional liming with bating (Figure 3 and 4).

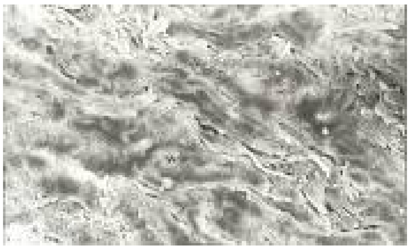

Figure 1. SEM image of cross-section of skin treated to CL. (200x Magnifications)

Figure 2. SEM image of cross-section of skin treated to CLB. (200x Magnification)

Figure 3. SEM image of cross-section of skin treated to LHP. (200x Magnification)

Figure 4. SEM image of cross-section of skin treated to LHPB (200x Magnification)

4. CONCLUSION

Tensile strength and elongation at break values of hydrogen peroxide applied leather samples were found in the close range of conventionally processed and bated leather samples. Bating process causes reduction in hide substance values of semi-finished and finished leathers by affecting particularly globular proteins. Likewise, hide substance content of hydrogen peroxide limed semi-finished leather was also decreased.

It is known that as a result of swelling of fiber structure during unhairing and liming processes and emerging of reactive groups, chrome tanning agent constitutes more bonds with collagen therefore the chromium oxide content of semi-finished leather is increases. The chrome oxide values of leather treated by hydrogen peroxide were higher than conventionally processed leathers. In trials where hydrogen peroxide and bating process were applied together, chrome oxide content of leather samples was found to be higher than hydrogen peroxide limed leather samples.

When the conventional liming is compared with hydrogen peroxide liming, it can be seen that COD and sulfide values of the hydrogen peroxide liming lower and lower than conventional one and hydrogen peroxide liming processes were more eco-friendly than conventional one.

When cross-section images of samples treated with LHP and LHPB were examined with scanning electron microscopy, no significant differences were found between SEM micrographs of the treatments. Removal of protein material between fibers and isolation of fibers can be seen in all applications.

Both hydrogen peroxide application and bating process have a decent effect on air permeability values of finished leather samples. Taking environmental hazardous effects into consideration, it is a must for leather industry to apply environmentally friendly chemicals and either to recycle or minimize wastes generated during processes in order to abide by continually altering, progressing and obligatory laws. To this end, revision of some chemicals used in conventional processes and processing technologies is inevitable.

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