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The Effect of Amphoteric Polymers on Dyestuff Consumption

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ABSTRACT

In recent years, the importance and use of wet-white tanning technology have increased due to the increase in environmental and health concerns. On the other hand, this technology still has problems related with fixation of dyestuff and fatliquoring agents during wet-end processes. In this study, the effect of the use of different commercial amphoteric retanning agents in different ratios on dyestuff consumption was investigated. For this purpose, amphoteric polymers were used at the beginning of dyeing process of syntan tanned leathers and the concentrations of remaining dyestuff after the process have been measured using UV-Vis Spectrophotometer for each trial. From the results it was concluded that the use of amphoteric polymers in retanning of wet-white tanned leathers significantly decreased the remaining dyestuff in the floats. Also, the physical and mechanical properties of the final leather were not adversely affected up to the use of 6 wt% the amphoteric polymer.

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Wet-White Tanning, Organic Tanning Agents, Amphoteric Retanning Agent, Dyestuff Consumption, Green Production

1. INTRODUCTION

Leather has been one of the most important natural fibrous materials used by humankind for apparel, shoe, upholstery, etc [1]. The production of finished leather consists of three parts: pre-tanning, tanning and post-tanning procedure, and finishing operation. Among these steps, tanning is usually considered to be the most important one [2]. In this process, the decomposable structure of raw skin/hide is transformed into a usable material that is a lot more stable to microbial attack and heat by using organic and inorganic compounds which react with the collagen protein of skin/hide [3]. However, tanning does not only transform the raw material into a physically and chemically stable material but also it defines the further reaction behavior and capacity of the leather [2].

In the tanning process, inorganic tanning agents (such as chrome, aluminum, zirconium) and organic tanning agents (such as vegetable and synthetic tanning agents, aldehydes, or their combinations) can be used [3]. Among these tanning agents, chrome tanning agent is the most widely used tanning agent in the leather industry for more than 100 years due to its many advantages and unique properties [4]. One of the most important reasons for the usage of chrome tanning agent is the strong affinity of chromium to collagen and the high reactivity of chrome-tanned leather to anionic retanning, dyeing and fatliquoring agents that confer handle, color properties, etc. to leathers [2,5].

On the other hand, the conventional chrome tanning process usually leads to high chromium (III)-containing wastes and effluents at the and of the process [6]. Moreover, there is a possibility that chromium (III) in the wastes and effluents may transform into chromium (VI) with the effects of various factors [3]. Although chromium (III) used as a tanning agent does not pose a significant health risk, the possibility of oxidation of free chromium (III) to chromium (VI) in leather products and wastes causes a potential risk in terms of human and environmental health. This circumstance constitutes the environmental and ecological agenda of the leather industry today [7,8].

As the current chrome tanning method does not meet the requirements for green production, environmental protection, and sustainability in the leather production, much more attention is paid to chrome-free leather production in recent years [9]. Particularly, vegetable/ syntan tanning system produces non-toxic solid wastes in splitting and shaving process and it completely prevents the

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risk of Cr (VI) formation [6]. However, organic tanning systems such as vegetable/syntan tanning reduces the positive charge of leather, and the isoelectric point (pI) of the leather is lower than chrome-tanned leathers. This is due to the polyphenolic structure of vegetable and synthetic tanning agents that their hydroxyl groups in the molecule react with the amino group of collagens by hydrogen bonding. The pI of syntan-tanned leather is around 4.2. Moreover, in the preparation of syntan, sulfonation is often used to modify polyphenols to improve its solubility. Sulfonic acid group of syntans can also interact with the amino groups of collagen by an ionic bond, which increases the negative charge in the skin [10]. Due to the blockage of amino groups and thus the decrease of pI, the binding capacity of vegetable/syntan tanned leathers for anionic chemicals decreases significantly [9,10].

The post-tanning process (retanning, dyeing, and fatliquoring) influences directly the final properties of the leather and thus, it is an important step for leather production. Anionic chemicals are commonly used in this process to improve the fullness, softness, flexibility, mechanical strength and color properties of the leather [11]. Therefore, when the anionic chemicals used in the post-tanning process cannot strongly bind to leather, these properties of the leather are affected adversely. As a result of this, leather quality decreases significantly [9,10]. Among the post–tanning chemicals dyestuffs are particularly important because they affect directly the aesthetic properties especially for the leathers such as nubuck and suedes. Acid dyes are the most commonly used dyestuff in post tanning processes since their penetration power and binding capacity is high and they are compatible with other anionic chemicals.

As a solution for the fixation problems in metal-free leather production systems, it is possible to increase the consumption of anionic wet end chemicals by using amphoteric polymers in the post-tanning process. In the literature there are studies related with the use of amphoteric agents in leather processing. Jia et al. [12] synthesized an amphoteric polymer agent to reduce the amount of total dissolved solids remaining from the leather production process and they used this agent as pickling aid agent and pre-tanning agent at the pickling process. The effect of amphoteric polymer on the amount of Cr_2O_3 bound by the leather and the distribution of chromium in collagen fibers were investigated. Xu et al. [2] synthesized reactive amphoteric polyurethane with multialdehyde groups and then used as a retanning agent to explore its effects on leather fibers. Liu et al. [13] synthesized oxidized valonia extract modified collagen retanning agent as an amphoteric retanning agent and they investigated the effects on shrinkage temperature, thickness, mechanical properties, dyeing properties and free formaldehyde removal function. Hao et al. [9] synthesized a high-performance amphoteric fatliquoring agent to match chromium-free tanning systems using the free radical copolymerization method with different monomers. They investigated the consumption of the amphoteric fatliquoring agent that they synthesized and the consumption of anionic dyestuff after the use of this agent. They all concluded in positive effects of amphoteric agents on fixation of anionic chemicals.

In this study, different type and ratios of selected commercial amphoteric polymers have been used in retanning process of syntan tanned leathers and their effect of on dyestuff consumption as well as mechanical and color properties were investigated.

2. MATERIAL AND METHOD

2.1. Material

For the dyeing trials with amptoheric polymers, wet-white leathers tanned with a replacement synthetic tanning agent (Blancotan HN, Silva, İtaly). The synthetic tanning agent (syntan) used in the study was based on phenol-naphtalane-sulfonic condensation product with a high tanning power. Pickled sheep skins were used in the study and the wet-white tanning process was given in Table 1. Subsequent to tanning process five different commercial amphoteric retanning agents were used in retanning/dyeing process and the details of the amphoteric agents were summarized in Table 2. For the dyeing experiments an anionic acid dye (Sellacid Blue PF, CI Acid Blue 25, TFL) was used. Other necessary chemicals used in processes were supplied from different leather chemical companies on the market.

Table 1. Wet-white tanning process using synthetic tanning agent

Process	Amount (%)	Chemical	Temperature (ºC)	Time (min)	pH
Depickling	150	Water, 7 ºBe NaCl	25		
	1	HCOONa		15	
	X	$NaHCO_3$		30	4.5
Wash&drain					
Tanning	100	Water	30		
	5	Syntan		20	
	10	Syntan		20	
	10	Syntan		20	
	1.5	Synthetic fatliquor		180	
	0.5	Fungucide		Over night	
Fixation	1	HCOOH (1:10)		60	
	X	HCOOH (1:10)		30	4
Drain&Wash					

Table 2. Commercial amphoteric retanning agents used in the study

Amphoteric polymer	Active substance	Active matter content (wt.%)
I	Soluble acrylic polymer	40
II	Acrylic copolymer	35-38
III	Acrylic and butacrylic acid copolymer	27
IV	Acrylic copolymer	25
V	Acrylic copolymer	37

2.2. Method

2.2.1. Leather Processing with Amphoteric Retanning Agents

The retanning/dyeing/fatliquoring experiments were performed in two groups and the experimental design of the study was given in Table 3 and Table 4. In the first group, the effects of different amphoteric polymers on dyestuff consumption were investigated (Table 3). The same amount of amphoteric polymers was used based on their active agent. In the second group, the effect of different ratios of the amphoteric polymers on dyestuff consumption was investigated (Table 4). The chosen amphoteric polymer was used between 2-8 wt.% based on the weight of the leathers.

The dyeing process receipt including the use of amphoteric polymer was given in Table 5. Amphoteric polymer was used after neutralization and before introducing the dyestuff. At the end of the overall process, aliquot samples were taken from the remaining bath to be examined in the UV-VIS spectrophotometer. The processed leathers were dried, conditioned and toggled prior to the mechanical tests.

Table 3. Experimental design of the first trial group

Trial No	Amphoteric Retanning Agent	*Amount Used (wt%)
1	I	1.5
2	II	1.5
3	III	1.5
4	IV	1.5
5	V	1.5
6	Control	-

*Values were given based on active agent of amphoteric agents.

Table 4. Experimental design of the second trial group

Trial No	Amphoteric Retanning Agent	Amount Used (wt%)
1	II	2
2	II	4
3	II	6
4	II	8

Table 5. Retanning/dyeing/fatliquoring process recipe of trial groups

Process	Amount used (%)	Chemical	Temperature (ºC)	Time (min.)	pH
Neutralization	200	Water	30	5	
	2	Neutral syntan		30	4.5-5
Retanning/ Dyeing/ Fatliquoring	X	Amphoteric retanning agent		60	
	4	Dyestuff		45	
	5	Natural+synthetic faliquoring agent	45		
	3	Synthetic fatliquor			
	1	Phospholipid based fatliquor		45	
Fixation	1	HCOOH (1:10)		45	
	0,5	HCOOH (1:10)		45	4
Washing					

2.2.2. Characterizations

2.2.2.1. Determination of dyestuff consumption

50 mL aliquot samples were taken from the remaining baths at the end of the dyeing process and measured in the Shimadzu UV-1800 spectrophotometer to determine the concentration of dyestuff. For this, diluted dyestuff solution was scanned in the range of 360-750 nm in the UV spectrophotometer and 594 nm was found to be the maximum absorption wavelength for the dyestuff (Sellaset Blue HN) and other measurements were carried out at this wavelength. For the sample measurements, a calibration curve was prepared with varied the concentration of dyestuff diluting by 1, 5, 10, 25 and 100 times from a stock solution of 0.15 g/L. The calibration curve was given in Figure 1. The aliquot samples collected from the dyeing floats were diluted, their absorbances were measured at 594 nm and the concentrations were calculated by using the calibration curve equation.

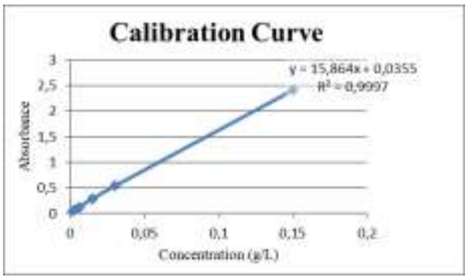

Figure 1. Calibration curve of the dyestuff and the curve equation

2.2.2.2. Color evaluation test of retanned leathers

Konica Minolta Spectrophotometer (model CM 3600d) was used to detect numerically the color coordinate values of leathers which retanned with amphoteric retanning agent. The colorimetric measurements were carried out on all trials according to CIE Lab color space. For the measurements the standard white plate was used as target and the average of 10 measurements from the grain side of the leather was given as L (lightness), a (red-green color coordinate) and b (yellow-blue color coordinate) color parameters for each trial.

In addition to this, ΔE (color difference value) was also calculated. In this color system, the ΔE formula calculates the linear distance between the coordinates of the sample color and the target color in the CIE Lab color space [14,15]. The target was determined as the leather retanned without an amphoteric retanning agent. The increase in ΔE means increasing the color difference between the target color and the sample color. The formula is given as Equation (1).

$$\Delta E = \sqrt{(L_{sample} - L_{target})^2 + (a_{sample} - a_{target})^2 + (b_{sample} - b_{target})^2} \quad (1)$$

2.2.2.3. Determination of the physical-mechanical properties of leathers

To evaluate the effect of the amphoteric retanning agent on physical-mechanical properties of leathers shrinkage temperature [16], tensile strength, elongation percentage [17], tear load [18] and grain strength [19] tests were carried out according to the official standard methods.

3. RESULTS AND DISCUSSION

3.1. Results of Dyestuff Consumptions

At the beginning of the experiments different types of amphoteric polymers were used in a fixed ratio (Table 3) to evaluate their performance on dyestuff consumption At the end of the dyeing process samples were taken from the bath, diluted when necessary, and measured at UV spectrophotometer to calculate the concentration of the dyestuff. The remaning dyestuff concentration values of the trial group with different commercial amphoteric retanning agents were given in Table 6 and their photographic images were shown in Figure 2.

Table 6. The concentration values of the bath samples processed with different amphoteric polymers

Samples (After dyeing process)	Concentration (g/L)
I	0.24 ± 0.003
II	0.18 ± 0.001
III	0.21 ± 0.002
IV	0.23 ± 0.003
V	0.22 ± 0.005
Control (VI)	0.61 ± 0.004

Figure 2. The samples in the first trial group

From Table 6, it was observed that the concentration value of the sample without amphoteric retanning agent (Control –VI-) was 3 times higher than other samples. This is possibly because the amphoteric retanning agent has both amino and carboxyl groups, which can form extra bonding sites for the dyestuffs and thus increases the dyestuff consumption. In addition, it was seen that different commercial amphoteric retanning agents exhibited similar dyestuff consumption. Taking into account their performance, the second (II) amphoteric retanning agent was chosen for further trials to evaluate the effect of different polymer ratios on dyestuff consumption.

In the second group of trials (Table 4) the selected amphoteric retanning agent (II) was used in different ratios (2,4,6,8%) in the dyeing process. The aliquot samples were taken from the bath at the fifth minute after introducing the dyestuff and at the end of the dyeing process, diluted when necessary and measured at UV spectrophotometer to calculate the concentration of dyestuff. The calculated results were presented in Table 7.

From the Table it could be clearly observed that with the use of amphoteric agent the dyestuff consumption increased significantly at the end of the process. Moreover, the consumption of dyestuff was found to be proportional to the increasing amounts of the amphoteric retanning agent. For instance, the use of 8% of the agent reduces the remaining dyestuff concentration 12 times less compared to the control sample. Taking into account the concentration values calculated at 5th minute of the process the dyestuff the consumption could be calculated to be over 98% with the use of amphoteric polymers in the process showing its significant effect on dyeing.

3.2. The Evaluation of Leather Colors

The colorimetric coordinate values of the leathers retanned with different commercial amphoteric retanning agents were given in Table 8 and the images of the leathers were shown in Figure 3.

According to Table 8, it could be seen that all leathers processed with amphoteric retanning agents showed a color difference (ΔE) comparison to the control leather and the highest color difference was observed at sample II. When we look at the L, a, b values we can see that the difference in color was mainly due to the decrease in lightness (L) values of the leathers indicating an increase in darkness. The color difference value of the leather retanned with the amphoteric polymer number II was 5.5 times higher than other samples. This change in color could possibly be related to increased amount of dyestuff bonded to the leather with the help of amphoteric polymers and in the case of sample II possibly more on the surface of the leather.

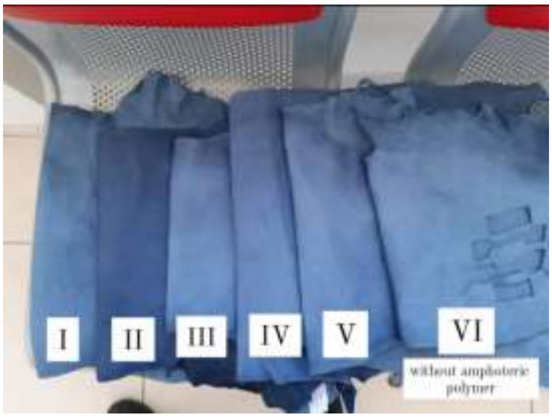

Figure 3. The leathers which were used different commercial amphoteric polymers

The colorimetric coordinate values of the leathers processed with different ratios of the amphoteric retanning agent were given in Table 9 and the images of these leathers were presented in Figure 4.

Figure 4. The leathers processed with different ratios of the amphoteric polymer

Table 7. The dyestuff concentration values of bath samples before and after the process

Amount of the amphoteric retanning agent (wt%)	Concentration at the fifth min of the dyeing process (g/L)	Concentration at the end of the dyeing process (g/L)
0	6.01 ± 0.012	0.61 ± 0.008
2	6.02 ± 0.018	0.11 ± 0.009
4	6.26 ± 0.015	0.08 ± 0.003
6	6.26 ± 0.019	0.07 ± 0.001
8	6.56 ± 0.013	0.05 ± 0.003

Table 8. The colorimetric coordinate values of the leathers that were used different amphoteric polymers

Sample	L	a	b	*Colour difference (ΔE)
I	43.89	-2.42	-15.62	1.32
II	33.88	-1.25	-15.06	11.40
III	42.84	-2.35	-15.72	2.36
IV	41.74	-2.27	-15.94	2.18
V	42.76	-2.38	-15.46	2.47
VI (Control)	45.20	-2.46	-15.77	-

* The leather retanned without amphoteric retanning agent (VI) was used as target

Table 9. The colorimetric coordinate values of the leathers that were used different amphoteric polymers in different ratios

Sample	L	a	b	*Colour difference (ΔE)
0%	45.20	-2.46	-15.77	-
2%	37.18	-1.55	-16.90	8.15
4%	31.04	-0.53	-15.39	14.30
6%	32.04	-0.95	-15.87	12.95
8%	27.20	0.13	-13.95	18.27

*Target was determined as the leather retanned without amphoteric retanning agent

The results from the Table 9 showed clearly the drastic change in color values of the leather with increasing amount of amphoteric agent. It could be observed that ΔE values increased and L values decreased significantly with increasing ratios of the amphoteric agent indicating darker colors for leathers.

3.3. Shrinkage Temperature

The effect of the amphoteric polymer on the shrinkage temperatures of the syntan tanned leathers was evaluated and the results were given in Table 10.

Table 10. The shrinkage temperatures of the leathers processed with different ratios of the amphoteric polymer

Sample	Shrinkage Temperature (^{o}C)
Syntan tanned leather	67.0±0.5
2% amp. pol.	68.5±0.5
4% amp. pol.	68.5±0.5
6% amp. pol.	69.0±0.5
8% amp. pol.	69.5±0.5

From the Table the shrinkage temperature of syntan tanned leather was calculated to be around 67 ˚C, which slightly increased with the use of amphoteric polymer at its increasing ratios indicating the positive effect of amhoteric polymers on the stabilization of collagen.

3.4. Mechanical Properties

Results of the tensile strength, elongation percentage, tear load values and grain strength of the leathers that processed with different ratios of the amphoteric retanning agent were given in Table 11.

According to Table 11, it was seen that the tensile strength of leathers was increased with the use of 2% and 4% amphoteric retanning agent. However, further increase in ratio of the amphoteric retanning agent (6 and 8%) led to decrease in tensile strength values. Similar behavior was also observed for the grain strength test and elongation percentage values. Up to the ratio of 4% amphoteric polymer use, the grain crack and ball burst strength of the leathers increased significantly, however, at the use of 6 and 8% the strength values decreased drastically. These results could be due to the accumulation of the polymeric agent on the surface of leathers when it is used excessively. It could also be observed that the tear strength of the leathers slightly decreased with the use of amphoteric polymer for all its ratios.

4. CONCLUSION

Present study highlights the effect of amphoteric polymers used in dyeing process of syntan tanned leathers. From the overall results it could be clearly stated that the use of amphoteric polymer significantly increased the dyestuff consumption. With the use of 8% amphoteric polymer the dyestuff consumption could reach even over 99%. From this point, the use of amphoteric polymers in wet-end processes helps to decrease the remaining dyestuff in the float and thus decreasing the pollution load of the wastewater as well as minimalizing the cost of dyestuff.

Moreover, the physical and mechanical properties of the final leather were not adversely affected up to the use of 6%, while the color intensity was increased with the use of amphoteric polymers. As a conclusion, it can be expressed that the use of amphoteric polymer in the retanning process of wet-white and metal-free leathers constitutes an important role for the fixation problems of anionic wet end chemicals which limits this technology. Taking into account the results related with both dyestuff consumption and leather quality parameters the offer of 4% amphoteric polymer seems optimal for its use in wet-end process.

Table 11. The tensile strength, elongation percentage and tear load values of the leathers

Sample	Max Load (N)	Tensile Strength (N/mm^2)	Elongation (%)	Tear Load (N)	Thickness (mm)	Grain Crack Strength (N)	Distention at grain crack (mm)	Ball Burst strength (N)	Distention at burst (mm)
0%	191.34±25.70	15.82±3.24	86.70±28.71	62.09±3.01	1.23±0.07	22.0±4.0	10.7±0.65	28.0±2.5	12.0±0.55
2%	214.96±23.51	16.73±3.11	82.41±24.62	54.53±3.36	1.30±0.05	29.5±3.0	11.4±0.30	31.5±1.6	11.9±0.35
4%	204.74±21.22	17.41±2.72	73.41±22.84	53.69±2.55	1.15±0.05	31.5±2,7	11.0±0.35	34.5±4.5	12.0±0.25
6%	121.97±20.54	11.16±1.68	65.23±25.67	34.81±2.62	1.07±0.04	8.0 ± 2.0	8.8±0.32	16.5±1.5	10.6±0.15
8%	150.14±22.35	13.22±2.14	70.41±20.66	52.63±3.23	1.14±0.06	9.0 ± 3.1	8.7±0.45	14.0±0.5	10.3±0.15

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