REDUCING THE AMOUNT OF TANNING MATERIALS PASSING INTO WASTEWATER IN POST-TANNING PROCESSES

by
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ABSTRACT

This research was carried out in order to detect and reduce the amount of the tanning material passing from leather into the float during post-tanning processes. In the research, the possibility of reducing the amount of unbound or weakly bound tanning materials, passing from leather into wastewater during post tanning processes, by forming a complex with a second tanning material used in a new float was examined. The feature of mineral tanning materials that enables them to form a complex with vegetable tanning materials was used for this purpose. It was proved that the amount of the mineral tanning material passing into wastewater during post tanning processes was reduced to some extent with vegetable tannin application after mineral main tannage, while the amount of vegetable tanning material passing into wastewater could be reduced in significant amounts of approximately 85% with mineral tanning material application after vegetable tannage.

INTRODUCTION

Leather processing is characterized by a large amount of solid and liquid waste (30-35 l/kg rawhide) and the removal of these wastes causes big problems for leather industry.[1,2,3] Several researches have been conducted in this respect concerning leather process steps, especially tanning process that causes significant pollution.

The tanning process can be defined as the conversion of a biological material, which is putrescible, into a material that is resistant to microbial attacks and has increased resistance to wet and dry heat.[4] Materials such as vegetable, mineral and synthetic are used to tan. Chrome, among mineral tanning materials, is the most widely used tanning material in leather production due to the unique features that it gives to leather. Besides chrome, aluminium and vegetable tanning materials are also widely used in leather production. An amount of tanning material remains in the float due to the reason that excessive amount of tanning material is used during the tanning process, or the process is not carried out properly. It is also known that some unbound or weakly bound tanning material remain within leather fibres, and these pass into the float during washing and other processes following tannage and are discharged to the environment through wastewaters. These unbound tanning materials share the same negative effects with the main tanning wastes, and the discharge of such wastes threatens both environmental and human health.

Although the methods of recycling chrome are well known and applied, pollution related to chrome continues to be one of the most important problems in leather industry.[5,6] Chromium compounds are among dangerous wastes, and they have several harmful impacts on soil, water and living beings due to their toxic effects. For example, Cr(III) content between 10-100 ppm in soil affects the microorganism population and reduces CO_2 formation, therefore it affects the biological reactions in soil in the negative way. Wastewaters that include chrome reduce the efficiency of the soil when discharged to agricultural land, and prevent the growth of the plants in these lands. Chromium compounds, especially Cr(VI), penetrate into the cell walls in living beings and cause mutagenic effects on nucleic acid. Therefore, they cause genetic corruption. In addition, over the long term they cause lung cancer, nephritis in kidneys, and respiratory tract mucous. Furthermore, such wastewaters, when discharged to watercourses, cause the living population in water to be poisoned, and the pollution they create destroys the balance in water environment.

Despite the possibility that aluminium may carry greater environmental risks than Cr(III) due to its high solubility, its environmental benefits or risks are not very clear when it is in combination with other tanning materials.[7]

Vegetable tanning materials, which are used in both tannage and retannage processes during leather production, are organic compounds containing phenolic groups that react with leather protein. These polyphenolic compounds, which pass into wastewater during the processes, do not decompose easily and they are highly toxic and dangerous organic pollutants.[8,9,10] By discharging the waters containing high concentrations of phenolic material to receiver environment, undesirable changes occur in biologic life. For example, it has been detected that physical circulation of N and P is prevented and mineralization of the organic materials in soil is reduced when polyphenol amounts that pass into soil exceed 3%.[11] At the same time, it is known that 6-7 mg/l of phenol concentration in waters has lethal effects on fish.[12] Legal limitations for tanning and finishing processes concerning the discharging of wastewaters that contain phenolic compounds were restricted to 4.5-5.5 mg/l.[13]

For these reasons, in order to reduce the amount of the tanning material which remain in residual float after tannage, precautions were and have being taken such as the utilization of pre-tanning materials that increase the consumption of tanning materials, reusing the residual tanning floats, ending the tanning process at different pH values and developing tanning materials with high consumption rates.[14] Certain progress was made regarding this matter, however, waste waters containing tanning materials does not occur only at the end of tannage. Also in wet processes applied after tannage, the tanning materials, which are not chemically bounded to the skin, kept in inter fibrillar area or weakly bounded to the skin, continue to pass into wastewater in the following steps of the process by the effect of mechanical action and water. Yet, after consulting the relevant literature, it has been observed that there does not exist any specific study carried out either on the amount of tanning material passing into the float through skin fibres after tannage, or on ways of reducing this amount. Several methods aiming at purifying tannery wastewaters have been developed and applied; however, it is more important to prevent the formation of wastes in tanneries.[3,15] In the research we carried out, which depends on today's clean technology standards and relies on the idea that preventing is better than reusing, reusing is better than recycling and recycling is better than discharging,[16] we aimed to reveal the pollution resulting caused by tanning materials that appear in post-tanning processes and reducing the source of the pollution by making use of the synergistic effect created by the main tanning material and a second tanning material that will be used in a new float.

Materials And Methods

Material

Sheep skin was chosen as research material and 20 pickled sheep skins of Persian origin were used.

Methods

Sheep skins were divided parallel at the back bone into two equal pieces, depickle, acidic bate, and fat removal processes were done according to the recipe given in (Table I).

The skins were randomly selected in 4 groups of 10 samples to be tanned by chrome (Cr) and aluminium (Al) from the mineral tanning materials, mimosa (Mi) from the condensed vegetable tanning materials, and valonea (Val) from the hydrolysables. The samples to be used for main tanning with chrome or aluminium were pickled to pH 3 with formic (1%, 30 min) and sulphuric acid (0.4%, 120 min) in 100% water (7°Bé). And the other samples to be tanned with mimosa or valonea were adjusted to pH 5 and 4.2 with formic acid in 100% water. Then the skins were tanned with the tanning materials (Table II, III). Samples were taken from the float at the end of the process, and tanning material concentrations and COD (chemical oxygen demand) values were detected in the residual float.

After the tanning process, samples were piled for 2 days, some of them were treated with water without using a second tanning material in order to be kept as blank (B) samples, and the amount of tanning material passing through the water was detected by taking samples from the float at the end of periods of 30, 60, 120 and 180 minutes.

TABLE I
General Formulation for Depickling, Bating and Degreasing Processes of the Samples

Process	%	Product	Temperature (°C)	Time (min.)	pH
Depickle	200	Water	25		
	10	Salt		10	
Pelts added	2	Sodium formate		30	
	1	Sodium bicarbonate		60	5.5-6.0
Drain					
Bate	200	Water	35		
	1	Acidic bate product		60	
Wash	200	Water		2x10	
Drain					
Degrease	5	Degreasing product		60	
Wash	200	Water		3x20	

TABLE II
Treatment with Vegetable Tanning Materials after Main Tannage with Mineral Tanning Materials

Main Tannage		Main Tannage	
2% Cr_2O_3	-	2% Al_2O_3	-
2% Cr_2O_3	+2% Val	2% Al_2O_3	+2%Val
2% Cr_2O_3	+2% Mi	2% Al_2O_3	+2% Mi

TABLE III
Treatment with Mineral Tanning Materials after Main Tannage with Vegetable Tanning Materials

Main Tannage		Main Tannage	
18% Val	-	18% Mi	-
18% Val	+0.25% Cr_2O_3	18% Mi	+0.25% Cr_2O_3
18% Val	+0.25% Al_2O_3	18% Mi	+0.25% Al_2O_3

Other samples were treated with a second tanning material in a new float after the main tanning process (Table II, III).

The purpose of this application was to reduce the pollution load that passed into wastewater by forming a complex between tanning materials. Cr and Al amounts in wastewaters were detected with Perkin-Elmer 2380 Atomic Absorption Spectrophotometer. Cr was measured at 357.9 nm by using air + C_2H_2 mixture; and Al was measured at 309.3 nm by using C_2H_2 + air + N_2O gases and at 0.7 slit intervals. The amounts of phenolic materials resulting from the vegetable tannins, and COD values were detected with Merck SQ 300 Water and Wastewater Spectrophotometer by using standard kits (Merck). Cr-phenolic material and Al-phenolic material complexes in wastewater samples, which appeared as the result of using the second tanning material for obtaining synergistic effect after the main tanning process, were precipitated by using NaOH solution (Cr at pH 7.5, Al at pH 6.5) in order to separate Cr and Al from phenolic complexes and to make a precise measurement ($Cr(OH)_3$ $Ksp=10^{-30.2}$, $Al(OH)_3$ $Ksp=10^{-31.7}$).[17,18] Finally, their measurements were made after the centrifuge. Additionally, shrinkage temperatures of the leather samples were determined according to SLC 406.[19]

Results And Discussion

The experimentally determined data contained in the tables and figures below are the average values of three replications.

Findings Belonging to Mineral Tanning Material Usage after Main Tanning with Vegetable Tannins

When the data obtained from the research was examined, it was found that 2.21 mg/l of phenolic material remained in the float at the end of main tannage with mimosa. It has been detected that there was 1.95-2.23 mg/l of phenol passing into float from leathers treated with only water as blank samples within a period between 30 to 180 minutes at the end of main tannage with mimosa (Table IV). It can be seen that the amount of tanning material that passed into wastewater from the leather during post-tanning processes is very close to the amount of waste tanning material which remains in the float at the end of tannage. This reveals the fact that a significant amount of polyphenolic material passes into wastewater during the processes applied after vegetable tannage.

TABLE IV
Average Values of Wastewater Analysis of Cr and Al Usage after Main Tanning with Mimosa

	Phenol (mg/l)	Cr (mg/l)	Al (mg/l)	COD (mg/l)
Mimosa Tannage	2.21	-	-	12970
Mi-B. 30′	2.23	-	-	7790
Mi-B. 60′	2.16	-	-	6920
Mi-B. 120′	2.05	-	-	6945
Mi-B. 180′	1.95	-	-	6590
Mi-Al 30′	0.68	-	18.7	6760
Mi-Al 60′	0.43	-	19.06	7180
Mi-Al 120′	0.42	-	12.71	7400
Mi-Al 180′	0.31	-	20	7360
Mi-Cr 30′	1.93	276	-	6345
Mi-Cr 60′	2.13	232	-	6705
Mi-Cr 120′	2.30	124	-	6525
Mi-Cr 180′	1.97	84	-	6760

It has been detected in the research that chrome, which was used for reducing the amount of phenolic material passing into the float in the following processes after main tanning with mimosa, does not have a significant effect on the rate of phenolic material passing into waste float. Additionally, it has been observed that, after main tanning with mimosa, the amount of phenolic material in waste float decreases depending on the period when Al is used instead of Cr and this amount decreases to 0.31 mg/l in the float at the end of 180 minutes. In this way, a decrease of 85% according to the amount of the tanning material (1.95 mg/l) that passed from unprocessed sample was achieved (Figure 1).

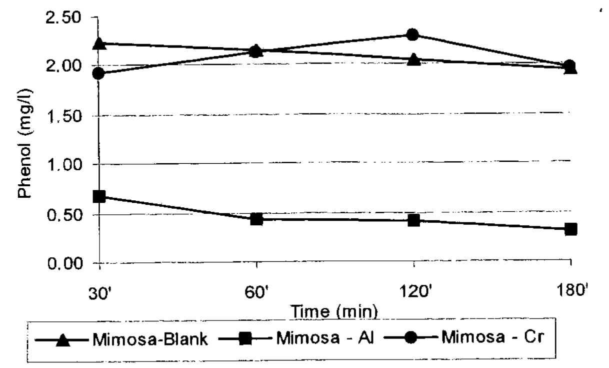

Figure 1. - Wasterwater Phenolic Material Values of Mimosa Main Tanned Samples

Wastewater samples were taken from the float within the same periods, and the chemical oxygen demand and the amounts of additional tanning material remaining in the float after the process were detected (Figure 2, 3).

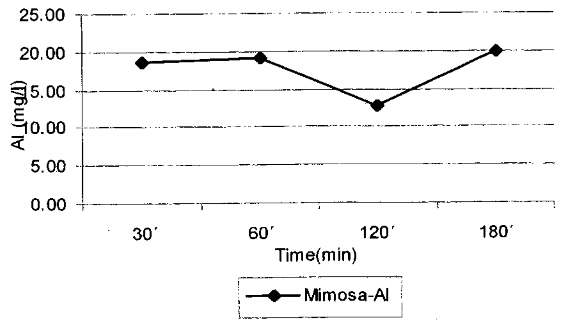

Figure 2. - Wastewater Al Values of Mimosa-Al Application

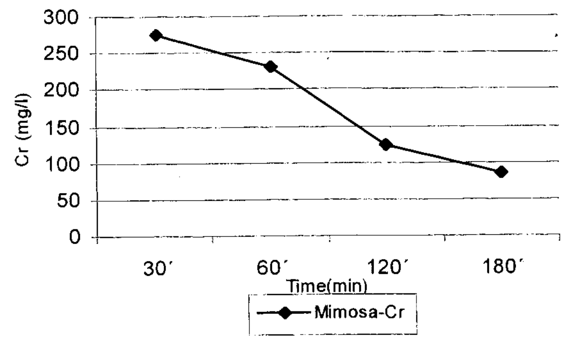

Figure 3. - Wastewater Cr Values of Mi-Cr Application

The findings indicated a decrease in the amount of phenolic material in the float, and it was determined that the pollution load (COD) of wastewater increased approximately 2.5-10% after main tanning with mimosa compared to the wasterwaters of blank samples.

In the research, it was found that wastewater containing 4.98 mg/l phenolic material arose at the end of main tanning with valonea, and an amount of 4.06 mg/l of additional phenolic material passed into the wastewater during the processes if no precautions were taken (Table V). However a decrease of 65% in the amount of phenolic material that passed into the float was observed by using 0.25% Cr_2O_3 in a new float after main tanning with valonea.

TABLE V
Average Values of Wastewater Analysis of Cr and Al Usage after Main Tanning with Valonea

	Phenol (mg/l)	Cr (mg/l)	Al (mg/l)	COD (mg/l)
Val. Tanage	4.98	-	-	30040
Val-B. 30	2.33	-	-	4860
Val-B. 60	2.92	-	-	5000
Val-B. 120	3.89	-	-	8680
Val-B. 180	4.06	-	-	7220
Val-Al 30	0.74	-	13.27	4790
Val-Al 60	0.58	-	7.1	5160
Val-Al 120	0.79	-	5.05	6650
Val-Al 180	0.72	-	4.48	6550
Val-Cr 30	1.90	304	-	5150
Val-Cr 60	1.77	160	-	5250
Val-Cr 120	1.93	92	-	5830
Val-Cr 180	1.45	52	-	5830

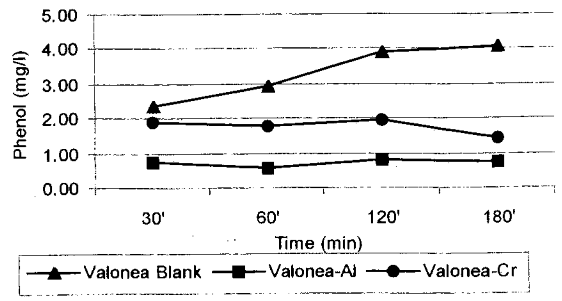

Figure 4. - Wastewater Phenolic Material Values of Valonea Main Tanned Samples

The most striking point in this observation is that the amount of phenolic material passed into the float was reduced to 0.72 mg/l with 0.25% Al_2O_3 usage after main tanning with valonea and this meant a significant rate of approximately 82% decrease as in mimosa application (Figure 4). Besides, it was discovered that COD values of wastewater decreased at a rate of 10-20% compared to the wastewater COD values of blank samples. Figures 5 and 6 show the amounts of Cr and Al that remain in wastewater.

Findings Belonging to Vegetable Tanning Material Usage after Main Tanning with Mineral Tanning Materials

When the data belonging to the leathers tanned with chrome was examined, it was found that 636 mg/l Cr remained in the float at the end of tanning process (Table VI).

After Cr tannage, it was detected that 260-328 mg/l of Cr passed into the float in a period between 30 and 180 minutes. After the main tanning process, neither valonea nor mimosa applications in the new float caused an effective decrease in the amount of Cr that passed into the wastewater, besides they increased the pollution load of the wastewater (Figure 7, 8).

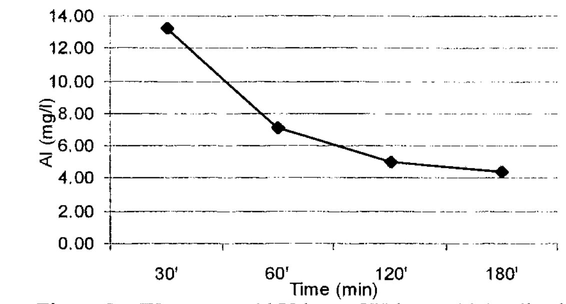

Figure 5. - Wastewater Al Values of Valonea-Al Application

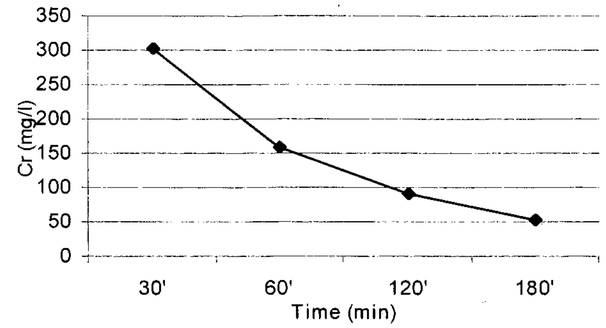

Figure 6 - Wastewater Cr Values of Valonea -Cr Application

TABLE VI
Average Values of Wastewater Analysis of Valonea and Mimosa Usage after Chrome Tannage

	Phenol (mg/l)	Cr (mg/l)	COD (mg/l)
Cr Tannage	-	636	11050
Cr-B 30′	-	304	880
Cr-B 60′	-	328	995
Cr-B 120′	-	284	1590
Cr-B 180′	-	260	1465
Cr-Val 30′	1.29	300	2485
Cr-Val 60′	0.95	288	2375
Cr-Val 120′	1.51	252	3305
Cr-Val 180′	1.27	228	3365
Cr-Mi 30′	1.58	320	1805
Cr-Mi 60′	1.81	216	2110
Cr-Mi 120′	1.72	272	2880
Cr-Mi 180′	1.79	276	2600

When the data in Table VII was examined, 2585 mg/l of Al was detected in tanning waste float at the end of the main tanning with aluminium. In addition, it was seen that 227.8 - 382.6 mg/l of Al passed into wastewater from the leathers, which were processed only with water without using a second tanning material for synergistic effect. The amount of Al passing into wastewater was found to be 212.8-302.4 mg/l for valonea application and 231.4-295.6 mg/l for mimosa application indicating that neither valonea nor mimosa application in a new float following main tanning with aluminium caused an effective Al decrease.

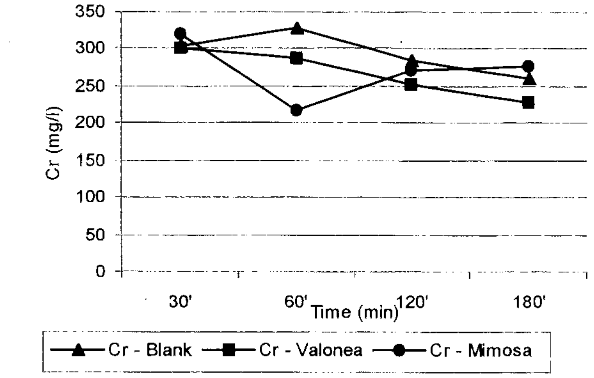

Figure 7. - Wastewater Cr Values of Cr Main-Tanned Samples

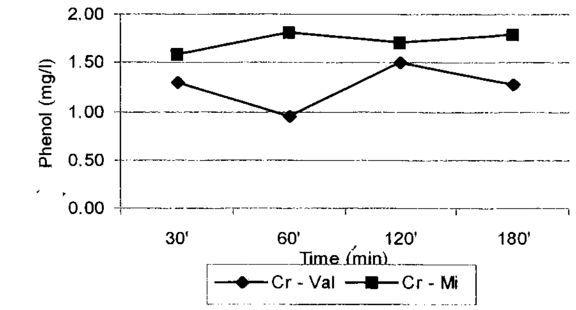

Figure 8. - Wastewater Phenolic Material Values of Cr Main-Tanned Samples

TABLE VII
Average Values of Wastewater Analysis of Valonea and Mimosa Usage after Aluminium Tannage.

	Phenol (mg/l)	Al (mg/l)	COD (mg/l)
Al. Tannage	-	2585	12900
Al.B 30′	-	382.6	1260
Al-B 60′	-	353.6	1640
Al-B 120′	-	242.2	1960
Al-B 180′	-	227.8	2040
Al-Val 30′	2.20	300.6	2820
Al-Val 60′	2.26	302.4	2080
Al-Val 120′	2.23	243.6	2520
Al-Val 180′	2.16	212.8	2410
Al-Mi 30′	3.47	289.2	2400
Al-Mi 60′	3.77	295.6	2120
Al-Mi 120′	4.02	234.4	2540
Al-Mi 180′	4.11	231.4	2700

In the light of this data, it was observed that the amount of tanning material passed into wastewater after Al tanning

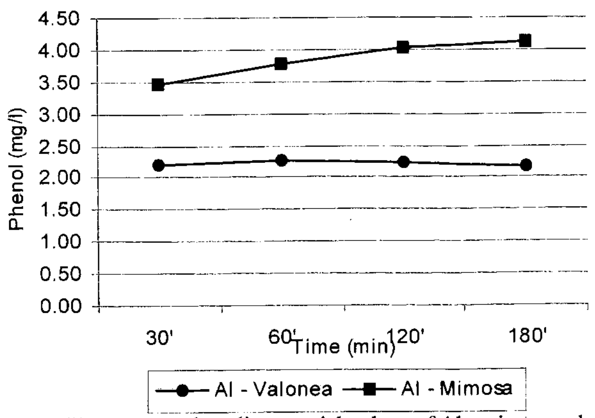

Figure 9. - Wastewater phenolic material values of Al main tanned samples

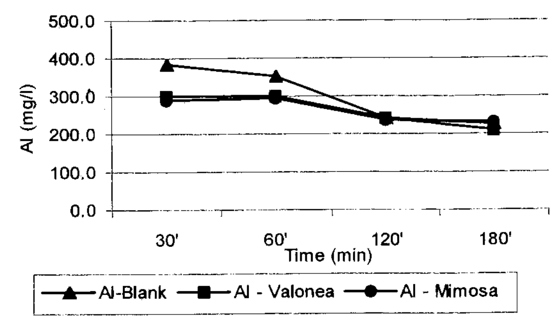

Figure 10. - Wastewater Al values of Al main tanned samples

process was rather high. This application also showed that wastewater COD values increased 18% when valonea was used and 32% when mimosa was used after main tanning process.

We discovered also in our research that there was an effective increase in shrinkage temperature as a result of the treatment with aluminium in leather samples which were tanned especially with vegetable tanning materials (Table VIII). As it is known, this increase in the shrinkage temperature depends on the complex-forming features of vegetable tanning materials and aluminium salts considered as synergistic effect (Figure 11).

Synergetic effect promoted especially with vegetable tanning materials and aluminium, and the studies carried out on Mi-Al and Val-Al combinations have showed that the shrinkage temperature, which is one of the tanning effect criterion, approached 100 °C and even exceeded this temperature values.[20,21]

TABLE VIII
Average Shrinkage Temperatures of Leather Samples

Main Tannage		Ts (°C)
2% Cr_2O_3	-	99
2% Cr_2O_3	+2% Valonea	109
2% Cr_2O_3	+2% Mimosa	105
2% Al_2O_3	-	72
2% Al_2O_3	+2% Valonea	72
2% Al_2O_3	+2% Mimosa	76
18%Valonea	-	73
18%Valonea	+0.25% Cr_2O_3	90
18%Valonea	+0.25% Al_2O_3	94
18% Mimosa	-	82
18% Mimosa	+0.25% Cr_2O_3	91
18% Mimosa	+0.25% Al_2O_3	93

Conclusions

When the findings obtained from the research were examined, it was detected that great amounts of tanning material remained in floats at the end of all main tanning processes. Research data revealed that in vegetable tannage, some tanning material, whose amount was close to the value remainining in the main tanning float, passed into wastewater, however the amounts passed into wastewater were not this high in the wet processes applied after main tannage with chrome or aluminium. The greatest pollution load due to remaining tanning materials and the COD is considered to have occurred in the tanning float during the chrome and aluminium tannage. The precautions to be taken at this point are thought to be more effective in terms of reducing the tanning wastes. On the other hand, it was found in this research that during the wet processes after vegetable tannage, there was an amount of passing as high as the amount of the waste tanning material remaining in the main tanning float. Therefore, the precautions concerning the reduction of the amount of tanning material, which will pass into wastewater during wet processes after tannage, are as important as the precautions to be taken during tannage. As a result of the research we carried out in order to reveal and reduce this amount, it was concluded that mimosa or valonea, which were applied on chrome or aluminium tanned leathers did not cause an effective reduction in the amounts of tanning material passed into wastewater from the leather during post-tanning processes. However, depending on the complex formation shown in Figure 11, it is possible to effectively reduce the amount of phenolic material passing into wastewater by using a little amount of aluminium or chrome tanning material after main tanning with mimosa or valonea. Yet, although phenolic material amount was reduced as a result of chrome application after vegetable tanning, the amount of waste caused by chrome was found to be high (52 and 84 mg/l) and the amounts passing into wasterwater was detected to be rather low when aluminium was used (4.48 and 20 mg/l). In addition, the applied method partly reduced the COD values and increased the values of shrinkage temperature.

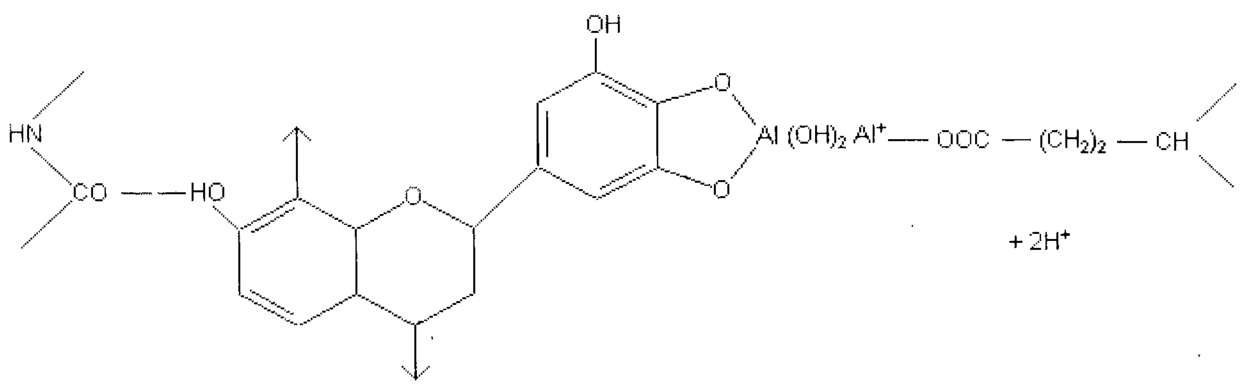

Figure 11. - Structure formula of mimosa-aluminium complex[22]

Notwithstanding the fact that the polluting effects of phenols are not dwelt upon in the leather industry as much as the effects of chrome, it is known that phenol and its derivatives are among toxic and dangerous organic pollutants and have negative effects on receiver environments. For example, phenolic compounds constitute a serious threat for the nature of high-quality waters due to their low organic decomposition rates.[23,24] If wastewaters mix with ground waters, even small amounts containing phenolic compounds may cause serious pollution in fresh water sources. More serious problems may arise when chlorine is used for disinfecting fresh water. When chlorine reacts with phenols, it forms chlorophenols which gives more harm to human health than phenol alone.[24,25] Considering the fact that such compounds prevent the physical circulation of N and P, and the mineralization of organic materials in soil and pose serious threat for the environment and living beings due to their toxic effects besides many other harmful reactions; the findings obtained in this research constitute significant outcomes, since it concludes that the amount of phenolic material passing into wastewater by aluminium application after valonea or mimosa tannage was reduced approximately 85%, while this amount was reduced 65% with chrome application after valonea tannage.

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