A New Pretannage with Glyoxal and N-Thioureidopyromellitamic Acid for High Exhaust Chrome Tannage

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Abstract

A new compound, N-Thioureidopyromellitamic acid, has been synthesized from pyromellitic dianhydride and thiosemicarbazide, and used in pretanning along with glyoxal to improve chromium uptake. The results show that the pretanned pelt has a higher shrink temperature than conventionally processed pelt and subsequent chrome tanning results in a significant increase in chromium uptake, and thus the chrome offer in conventional chrome tanning can be reduced in large amounts. Furthermore, because of higher shrink temperature of the pretanned pelt, the initial temperature of two stage chrome tanning is raised and thus a much higher exhaustion of chromium is obtained at the elevated tanning temperature. The handle and the physical properties of pretanned crust leather are not much different from those of crust leather made from pelts that were not pretanned.

Abstracto

Un nuevo compuesto, el ácido agotamiento del cromo que resulta debido a la más alta temperatura. Tanto el tacto, como las propiedades físicas del cuero recurtido no son muy diferentes de las de cuero recurtido desde pieles no precurtidas.

Introduction

Chrome tanning has been used as a commercial process since 1884 and is now the most commonly used tanning method worldwide. In conventional chrome tanning processes, about 20-30% of the chromium salts added are released into the effluent during tanning, which usually causes environmental problems. In order to reduce the release of chromium, many researchers and tanners have been striving to improve the processes. One of the routes with good potential for success is to introduce additional carboxyl groups into collagen by pretanning or pretreating pelts with some reagents in aqueous solution. The formation of additional carboxyl groups in collagen might be expected to enhance the chrome exhaustion by simply providing more sites for chrome binding. An amino acid (glycine) and malonic acid were used along with form aldehyde to couple carboxyl groups to collagen, and the results were found to be effective in increasing the shrink temperature and chrome uptake but their applications in tannery operation

tanning to introduce additional carboxyl groups to collagen. The conditions and the effectiveness of the pretanning have been investigated.

EXPERIMENTAL

Materials

Pyromellitic dianhydride, thiosemicarbazide, N,N-dimethylformamide, triethylamine, glyoxal and normal chrome powder (Cr_2O_3 26%) were purchased from Xian Chemical Company. Delimed goatskins (pH 8.5) were obtained from a local tannery. In all cases, percentages are based on an actual drained delimed weight.

Synthesis of N-Thioureidopyromellitamic Acid

Pyromellitic dianhydride (22.14g) was dissolved in 100 ml of anhydrous N,N-dimethylformamide and cooled to 10 °C. A solution of thiosemicarbazide (18.95g) in 100 ml of anhydrous N,N-dimethylformamide was added thereto in small portions with stirring. The mixture was agitated for another 10 minutes and 15 ml of triethylamine was added over a period of 20 minutes. The temperature was maintained at 5-15 °C.The crystallization of the amine salt of N-thioureidopyromellitamic acid occurred. The crystals were left to stand at 5 °C for 24 hours, then filtered, washed with N,N-dimethylformamide, anhydrous acetone and dried under IR-lamp.

The amine salt of N-thioureidopyromellitamic acid was dissolved in 500 ml deionized water at 5 °C. The solution was neutralized with 1 N HCl. The white crystallizations occurred immediately. The crystals were filtered, washed with deionized water and dried at 5-20 °C in vacuum dryer. The yield of dried product is 92.8%.

Pretanning of Pelts

In a typical laboratory scale experiment, 100 g of delimed pelts was continuously drummed in 40 ml water at 20° and 1.6-9.7 g of glyoxal solution (strength 30%) was added. After running for 6 hours, 1.7-5.0 g of N-thioureidopyromellitamic acid was added and drummed at 35-40 °C for another 12 hours. During the pretanning, the pH value of the bath was maintained at 7.0-8.0 by adding small amounts of $NaHCO_3$. At the end of the pretanning, the shrink temperature was determined and then the pelts were washed and pickled in 60 ml of sulfuric acid solution to pH 3.5.

Chrome Tanning

(a) Conventional chrome tanning

In the above pretanning bath, 2.5-6.0% of normal chrome powder was added and drummed for 90 minutes, and then 0.3% of MgO was added and run for another 2 hours. After the pH value of tanning bath attained 3.8~4.2, 100 ml of hot water (60-70 °C) was added to raise the temperature to 38-40 °C, and run for another 8 hours. In the end, the shrinkage temperature of the wet blue and the chromium content in effluent (200 ml) were determined.

(b)Two stage chrome tanning

In the first stage, the above pretanned pelt was drummed in 200 ml of spent chrome solution at 40 °C for 8 hours, and then the bath was analyzed and discharged. In the second stage, the wet blue tanned by first stage was drummed in fresh chrome liquor according to above conventional chrome tanning process and then the spent chrome solution was collected and reused for the first stage of subsequent batches. The shrink temperature of the wet blue and the chromium content in effluent were determined.

Dyeing and Fatliquoring

After neutralized to pH value 5.5-6.5, 100 g of wet blue was continuously drummed in 200 ml water at 50 °C and 3g of Remazol Deep Black N was added. After running for 40 min, 15g of fatliquoring agent was added and drummed at 50 °C for another 90 min. At the end of the fatliquoring the pH value of the bath was adjusted to 4.0 by adding small amounts of formic acid and run for 20 min. The dyestuff content in spent dyeing liquor was determined.

Analyses

UV spectrum was recorded in Shimadzu UV-160A UV-Vis spectrophotometer (5×10^{-5}mole/l, water) and IR spectrum was recorded in Nicolet Magna-IR550 spectrophotometer (KBr disc). EI-MS spectrum was run on Micromass GCT CA055 spectrometer.

Shrink temperature was determined by typical industry equipment. The strength of the crust leather was measured on an Instron Tester after the wet blue was neutralized, fatliquored, dried, staked and toggled.

Chrome content in spent solution was determined by atomic absorption spectroscopy. Chromium standard solutions with various concentrations were prepared by dissolving potassium dichromate in water, and the standard curve of the concentration versus the atomic absorbency was obtained at 357.9 nm. 50ml diluted spent solution was taken, and 5ml nitric acid and 2ml perchloric acid were added and boiled. Then 4ml of 2 mol/L ammonium chloride was added, and diluted to 100ml. The absorbency at 357.9 nm was determined on a Shimadzu AA-6501 atomic absorption spectrophotometer. The chromium content in the spent solution was calculated from the absorbency and the standard curve.

TABLE I
Shrink Temperature[b] and Chromium Exhaustion[b] of Pretanned Pelts

Trial[a] No.	Glyoxal (%)	UPMAA (%)	Ts after Pretanning, °	Ts after Tanning, °	Chromium in effluent (g Cr_2O_3/l)	Chromium Exhaustion (%)
Control	0	0	58±0.5	98±1.0	2.050±0.061	73.71±0.78
1	2.4	5.0	65±1.0	106±0.6	0.225±0.022	97.12±0.28
2	4.8	5.0	68±0.8	112±0.8	0.177±0.018	97.73±0.23
3	7.2	5.0	67±0.8	110±1.2	0.189±0.024	97.58±0.31
4	9.7	5.0	68±1.9	111±1.4	0.195±0.019	97.50±0.24
5	3.2	3.3	66±2.2	106±1.1	0.687±0.035	91.19±0.45
6	1.6	1.7	62±2.4	102±1.5	1.071±0.046	86.27±0.59

[a]Triplicate samples for each offer of glyoxal and UPMAA.
[b]The values represent triplicate measurements for each sample; hence each value represents nine measurements.

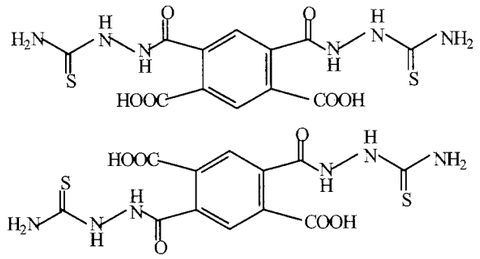

Figure 1. - Isomers of N-thioureidopyromellitamic acid

Dyestuff content in spent dyeing liquor was determined by visible spectroscopy. The standard curve of the dyestuff concentration versus its absorbency was obtained at 587 nm. The absorbency of spent dyeing liquor was determined on Shimadzu UV-160A UV-Vis spectrophotometer. The concentration of the dyestuff in spent liquor was calculated from the absorbency according to the standard curve.

RESULTS AND DISCUSSION

The mixing of pyromellitic dianhydride and thiosemicarbazide in the presence of triethylamine leads to the nucleophilic addition of thiosemicarbazide to pyromellitic dianhydride. The addition leads to the opening of the pyromellitic cycles and formation of amine salt of N-thioureidopyromellitamic acid. When acidified with hydrochloric acid, the amine salt gives N-thioureidopyromellitamic acid (UPMAA) that has two isomers as shown in Figure 1.

The structures of the compounds were elucidated by UV, IR and EI-MS. In UV spectra the compounds have two strong absorption bands at 202 nm and 242 nm. The IR spectra exhibited characteristic N-H bands at 3435, 3285, 3185 cm^{-1}, and amide C=O stretching bands at 1695 cm^{-1}, 1680 cm^{-1}. The IR spectra also showed carboxyl C=O stretching bands at 1715 cm^{-1}, and C=S absorption in 1245-1305 cm^{-1} region. In EI-MS of the compounds, no molecular ion was found because of its low stability. The acylthiosemicarbazide fragmented via two prominent pathways to afford the fragments at m/z 59 ($HN=C=S^{+\cdot}$) by NHNH-CS bond cleavage and hydrogen transfer; and the fragments at m/z 60 (H_2N-$C=S^{+}$) by CO-NH bond rupture.

Because of their active thioureido groups and carboxyl groups, these isomers can be coupled to collagen by

TABLE II
Effect of Chrome Offer on Shrink Temperature[b] and Exhaustion[b]

Trial[a] No.	Chrome powder (%)	Ts after chrome tanning (°C)	Chromium in effluent (g Cr_2O_3/l)	Chromium Exhaustion (%)
1	3.0	86±0.5	0.052±0.010	98.66±0.26
2	3.5	95±0.8	0.087±0.008	98.09±0.18
3	4.0	98±0.9	0.094±0.011	98.19±0.21
4	4.5	102±1.0	0.101±0.015	98.27±0.26
5	5.0	107±0.7	0.112±0.020	98.28±0.31
6	5.5	110±1.2	0.158±0.012	97.79±0.17
7	6.0	112±1.5	0.174±0.018	97.76±0.23

[a]Triplicate samples for each chromium offer.
[b]The values represent triplicate measurements for each sample; hence each value represents nine measurements.

TABLE III
Effect of Pretanning on Two Stage Chrome Tanning

Trial[a] No.	Glyoxal (%)	UPMAA (%)	Ts[b] after Pretanning, °C	Ts[b] after Tanning, °C	Chromium[b] in effluent (g Cr_2O_3/l)	Chromium Exhaustion[b] (%)
Control	0	0	58±0.5	102±1.0	0.981±0.015	90.56±0.13
1	2.4	5.0	65±0.8	110±1.6	0.151±0.011	98.55±0.14
2	4.8	5.0	68±1.1	116±1.2	0.086±0.014	99.17±0.18
3	7.2	5.0	67±1.2	112±1.8	0.103±0.021	99.01±0.27
4	9.7	5.0	68±1.6	113±1.0	0.091±0.013	99.13±0.17

[a]Triplicate samples for each offer of glyoxal and UPMAA.

[b]The values represent triplicate measurements for each sample; hence each value represents nine measurements.

glyoxal when they are used in pretanning, and thus additional binding sites for chromium can be introduced into pelts prior to chrome tanning.

In our initial experiments, a delimed goatskin was cut into pieces. The six pieces were pretanned with various amounts of glyoxal and UPMAA at pH 7-8, and one was used as the control. After washing and pickling to pH 3.5, the pretanned pelts and the control were tanned separately with 6.0% of normal chrome powder according to conventional process. Significant increases in the chromium uptake were found in the pretanned pelts over the control along with corresponding increases in the shrink temperatures (Ts).The results are reported in Table I. The optimum chromium absorptivity was obtained when the pelt was pretanned with 4.8% of glyoxal and 5.0% of UPMAA. Under this condition, the shrink temperature of the pelt was increased from 58 °C to 68 °C, and the shrink temperature of the wet blue was as high as 112 °C. These results indicate that new crosslinks and binding sites for chromium might be introduced into collagen by the pretanning, and imply that chrome offer could be reduced after the pretanning.

In order to optimize the chrome offer matched with above pretanning, the pelts were tanned with various amounts of normal chrome powder after pretanning with 4.8% of glyoxal and 5.0% of UPMAA, and the results are shown in Table II. When the chrome offer was reduced from 6.0% to 3.0%, the shrink temperature was remarkably reduced from 112 °C to 86 °C and the chromium absorptivity was slightly increased from 97.8% to 98.7%. Considering customer's demands on shrink temperature, 3.5-4.0% of normal chrome powder was taken as the optimum offer.

Delimed pelts were pretanned with various amounts of glyoxal and 5.0% of UPMAA at a pH of 7-8, and then pickled and tanned with 6% of normal chrome powder according to two stage process, the results are shown in Table III. After pretanning, the shrink temperatures of the pelts were increased from 58 °C to 65-68 °C. This makes it possible to carry out the first chrome tanning with spent chromium solution at an elevated temperature (40 °C). Because of the elevated tanning temperature as well as the introduction of new binding sites, a much higher exhaustion of chromium was obtained during the two stage chrome tanning (Table III). These show that pretannage with glyoxal and UPMAA is very suitable for two stage chrome tanning

In order to evaluate the pretanning further, full goatskins were cut into two sides along backbone. One side was pretanned with 4.8% of glyoxal and 5.0% of UPMAA in pH 7-8, and another was used as the control. In one experiment, the pretanned side and the matched control were pickled to the same pH value and tanned with 6.0% of normal chrome powder according to conventional process. In another experiment, the pretanned side was tanned with 4.0% of normal chrome powder and the matched control was tanned with 6.0% of normal chrome powder according to conventional process. All the wetblues were dyed and processed into crust leather. The dyestuff exhaustion and the physical properties of the crust are shown in Table IV. The appearance and handle of pretanned side were not much different from those of control. The physical test values and the dyestuff exhaustions indicate that there is no significant difference between the pretanned sides and the controls, particularly between the side with reduced chrome offer and its matched control, except for a reduction in extension. Therefore, the reduced offer can be achieved with no significant change in leather properties by the pretanning.

TABLE IV
Dyestuff Exhaustion[a] and Crust Properties[a]

Trial No.	Control 1 (6% chrome powder)	Pretanned 1 (6% chrome powder)	Control 2 (6% chrome powder)	Pretanned 2 (4% chrome powder)
Dyestuff Exhaustion (%)	85±1.26	88±1.14	85.5±1.08	82±1.19
Tensile strength (N/mm^2)	23±1.8	23±1.5	25.6±0.9	22±1.3
Extension at 5 N/mm^2 (%)	45±6.9	37±5.87	48±6.25	36±3.91
Extension at break (%)	93±8.32	77±6.76	86±7.49	72±5.12
Tear strength (N/mm)	50±5.94	51±6.14	55±5.34	54±4.39
Burst strength (N)	25.0±0.3	24.6±0.5	26.0±0.4	23.8±0.3

[a]Duplicate samples for each experiment; four measurements for each sample; hence each value represents eight measurements.

Conclusions

N-thioureidopyromellitamic acid (UPMAA) can be synthesized by the nucleophilic addition of thiosemicarbazide to pyromellitic dianhydride, and used along with glyoxal in pretanning to improve chromium uptake. The optimum proportion of UPMAA to glyoxal seems to be 2:1 mole that is corresponding to 4.8% of glyoxal and 5.0% of UPMAA. Under this condition, the shrink temperature of the pelts could be raised to 68 °C by the pretanning and subsequent chrome tanning would result in significant increases in chromium uptake and shrink temperature, and therefore, the chrome offer in conventional chrome tanning can be reduced by large amounts. Because of higher shrink temperature of the pretanned pelts, the initial temperature of two stage chrome tanning could be raised to 40 °C and thus a much higher exhaustion of chromium can be obtained. The handle and the physical properties of pretanned crust leather are not much different from those of crust leather made from pelts that were not pretanned.

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