

Hide Tanning with Modified Natural Tannins

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ABSTRACT: Tannin from “Acacia Mearnsii” usually called Mimosa, is largely employed in vegetal tanning of hide even if the quality of the leather is poorer than that obtained using chromium as tanning agents. However, taking into account the natural resources of this product and its reduced environmental impact, mimosa tannin has been modified to obtain leather having improved properties. Tannin was modified using formaldehyde, urea, a sulfonic acid and a sulfiting agent: The new products show a higher molecular weight than mimosa tannin but maintain a good solubility in water. Modified tannins were characterized through physicochemical and technological tests and evaluated as tanning agents. The properties of tanned leathers obtained using the new tannin products and mimosa were compared. Some of the polymers containing phenolsulfonic acid are good tannin agents, especially those with a suitable molecular weight. The technological and sensorial properties of the leather obtained using

modified tannins (distension and strength of grain, tensile strength, elongation, and tear load) are better than those obtained using mimosa when an appropriate ratio of the reagents were employed. At the same time the feeling of the tanned leather was improved and the final products show fullness, elasticity, fluency, reactivity, and a thin and fine grain. Some of the tannins modified with naphthalen-sulfonic acid show poor tanning properties but good penetration in the leather suggesting their use as auxiliary tannins in the pretanning process. A simple procedure to prepare these modified tanning agents in the course of the tannin extraction is suggested. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1797–1809, 2008

Key words: biomaterials; polyaromatics; polycondensation; high-performance polymers; water-soluble polymers; leather; modified tannin; formaldehyde; sulfonic acid; urea

INTRODUCTION

Tanning of hides or skins with plant extracts is an old technique largely employed in the past to produce many types of leather.^{1,2} Many plants produce tanning agents, present in their wood, bark, leaves, or roots from which they are extracted. Among these “Acacia Mearnsii,” usually called mimosa (a leguminose growing in a short time) has been largely used to obtain tanning extracts employed in the tanning of hide, due to their reduced environmental impact. More than one century ago vegetable tannins were substituted by chromium tanning agents because the final leather showed better technological and sensorial properties and today about 90% of the world’s leather production is obtained using chromium(III) technology. This process, however, suffers from many problems deriving from the high environmental impact of the by-products formed in these reactions, i.e., the typical limit for chromium is less than 5 ppm ($<10^{-4}$ M) in the waste. Furthermore new legislations concerning the control of pollution will

reduce these limits in the future. In addition, the request of consumers for natural or ecological leather is growing due to their improving sensibility to environmental problems.

The substitution of chromium with other tanning agents has been followed through many ways.^{2–5}

This research is devoted to satisfy a growing demand of new tanning products from modified natural tannins, able to substitute, totally or at least partially, the chromium tanning process. Aim of this study was to improve the tanning properties of mimosa tannin, which allow production of leathers having characteristics very close to those obtained with chromium tanning agents. The partial or total substitution of chromium may satisfy the request of leather tanned with natural products and will reduce pollution due to by-products formed in the chromium process.

Modified tannins were obtained through polymerization of mimosa tannin with a crosslinking agent, that is a process very close to that employed for the production of synthetic tannins. Some approaches using modified tannins are reported in the literature.^{6–9} In our procedure, tannin was modified using a sulfonic acid while formaldehyde and urea were chosen as crosslinking agents because their combina-

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tion may improve the tanning properties of the final product if correlated with those of natural tannin, especially the stability to light. The lack of this stability is in fact one of the negative aspects of natural tannin.

The new polymers must have the positive properties of synthetic tannins (leather with a white or pale color and a good stability to light) together with those of natural tannins (leather with a "natural" aspect, fullness, a thin and fine grain). Because the modified tannins are devoted to an industrial process a great attention has been paid to the cost of the process using cheaper materials, low transformation of the plants used for the extraction of tannins, and low environmental impact of the modified process.

EXPERIMENTAL

Instruments

The FTIR spectra were collected with a spectrophotometer Perkin-Elmer System 2000 using an ATR (attenuate total reflection) accessory (Golden Gate, SPECAC, UK) or KBr pellets.

Molecular weight determinations, based on the isopiestic method were performed using a Wescam mod. 233 osmometer.

HPLC analysis were performed using a modular instrument equipped with two C18 columns (25 cm length), a Perkin-Elmer (LC mod. 250) pump, a Rheodyne 7010 valve, a 200- μ L injection loop and a detector Perkin-Elmer LC 30 refractive index or a Perkin-Elmer diode array working at 255 and 280 nm.

A capillary Cannon-Fenske viscosimeter was employed in a thermostated water bath to evaluate the viscosity of the solutions.

Materials

The materials employed were commercial products and used as supplied, without any further purification.

Synterol BA: Alfa; Oxalic acid: Aldrich; Sodium formate: Aldrich; Intan C03: Alfa; Alfa 1150: Alfa; Brown CG color: Alfa; Formic acid: Aldrich. Phenolsulfonic acids: Aldrich; Naphtalensulfonic acid: Aldrich; Naphtolsulfonic acid: Aldrich; Fat-H50: Alfa.

Hyde of 3-years old rumanian cow was employed.

Polymerization procedure

A general procedure has been followed for each series of polymers. The polymerization has been carried out in acid media using the tannin/formaldehyde ratio reported in Table I at temperature of 85°C

with the aim to obtain a preferential condensation with respect to the methylation process. A reaction time higher than 10 h was adopted to facilitate the inclusion of sulfonic acid inside the polymers. The amount of reactants and the reaction conditions are reported in Table I.

Three polymerizations were carried out for the synthesis of each product and the mean values are reported.

Analysis of modified tannins

Solubility of polymers

a. Candle filtering method

This is the usual method employed to evaluate the solubility of tannin extracts, and the amount of not soluble products.^{10,11} In this method all no-filtered residue through a specific candle of porous ceramic material is considered as insoluble products. A ceramic candle (externally high 128 mm, internally high 123 mm, outer diameter 31 mm, inside diameter 21 mm) is introduced for 9/10 of its high in an aqueous solution containing 4 g/L of the product. The inside part of the candle is connected to a siphon. After 5 h the solution inside the candle is siphoned and collected. An equal amount of the starting and siphoned solution are placed in two capsules and dried for 12 h at 120°C obtaining a constant weight. The amount of the insoluble residue is determined by difference between the two weights.

b. Centrifugation method

This method assumes that the residue not dissolved in the solution may be separated through centrifugation. The solution prepared as above (4 g/L) is centrifuged for 30 m at 3500 rpm. An equal amount of the starting and centrifuged solution are placed in two capsules and dried for 12 h at 120°C obtaining a constant weight. The amount of the insoluble residue is determined by difference among the two weights.

Tanning substances

The method called "Filter method" or "Procter method" has been employed.^{10,11} This method assumes that no tanning substances are able to filter through a glass bell containing a leather powder tanned in standard conditions. Practically a glass bell (height 85 mm, diameter 28 mm), open at the two extremity and containing a standard amount of powder of tanned leather, is inserted in the tannin solution (4 g/L) for 9/10 of its high, and after imbi-

TABLE I
Products Employed for the Synthesis of Modified Tannins

Polymercode	Formaldehyde solution (g)	Urea (g)	Sulfonic acid*	Na ₂ SO ₃ (g)	Tannin/formaldehyde molar ratio	Formaldehyde/urea molar ratio
A1	0.54	0.15	A	–	6.12	2.59
A2	0.76	0.24	A	–	4.35	2.28
A3	0.98	0.29	A	–	3.37	2.44
B1	0.54	0.15	B	–	6.12	2.59
B2	0.76	0.24	B	–	4.35	2.28
B3	0.98	0.29	B	–	3.37	2.44
C0	0.00	0.00	C	–	//	//
C1	0.54	0.15	C	–	6.12	2.59
AS _p 1	2.18	0.61	A	5.00	1.52	2.58
AS _p 2	2.72	0.79	A	5.00	1.21	2.48
AS _p 3	3.27	0.94	A	5.00	1.01	2.51
AS _p 4	3.81	1.10	A	5.00	0.87	2.50
AS _c 1	2.18	0.61	A	5.00	1.52	2.58
AS _c 2	2.72	0.79	A	5.00	1.21	2.48
AS _c 3	3.27	0.94	A	5.00	1.01	2.51
AS _c 4	3.81	1.10	A	5.00	0.87	2.50
BS _p 1	2.18	0.63	B	5.00	1.52	2.49
BS _p 2	2.40	0.69	B	5.00	1.38	2.51
BS _p 3	2.72	0.79	B	5.00	1.21	2.48
BS _p 4	3.27	0.94	B	5.00	1.01	2.51
BS _c 1	2.18	0.63	B	5.00	1.52	2.49
BS _c 2	2.40	0.69	B	5.00	1.38	2.51
BS _c 3	2.72	0.79	B	5.00	1.21	2.48
BS _c 4	3.27	0.94	B	5.00	1.02	2.51

Tannin 40 g, sulfonic acid 14 g (water solution 60%), water 60 g, formaldehyde (water solution 36%).

* **A**: Phenolsulfonic acid; **B**: Naphtalensulfonic acid; **C**: naphtolsulfonic acid.

bition of the leather powder (3 h) the remaining solution is siphoned and collected. An equal amount of the starting and siphoned solution are placed in two capsules and dried for 12 h at 120°C obtaining a constant weight. The amount of the residue is determined by the difference among the two weights giving the amount of no tanning substances.

Molecular weight

The average molecular weights (M_n) of mimosa tannin and modified tannins were obtained with a water solution of the product using a vapor pressure osmometer. No preliminary treatment of the products was done. The calibration of the instruments was obtained using a water solution of glucose acetate.

IR spectroscopy

FTIR spectra of mimosa and modified tannins were collected using an ATR device or KBr pellets. The main absorptions are reported in Table II.

HPLC analysis

The HPLC was used to detect the progress of the polymerization. This method has been useful to evidence the change of the composition of the start-

ing solution in the course of the polymerization, even if the products present were not fully identified. A preliminary filtration through a nitrocellulose filter (porosity 0.45 μm) was adopted to avoid occlusion of the syringe or the column. A slightly modified procedure with respect to that reported for the analysis of tannin in wine was employed.¹² A water/methanol gradient was employed as eluent with the water acidified at a pH 2.5 by addition of perchloric acid. The number of peaks, their retention time and their form were checked and correlated with those of the starting solution.

A Mirabolano tannin (hydrolysable tannin) was also analyzed using this method.

Viscosity

The viscosity was detected using water solutions having a known concentration of the products with a capillary Cannon-Fenske viscosimeter at constant temperature.

Tanning of hide

Hide from 3-years old Rumanian cow, having a weight of 2–3 kg of humid leather was used, and the amount of products employed in the tanning process was referred to humid leather. The working process

TABLE II
Main IR Absorptions of Tannins

Mimosa tannin (cm ⁻¹)	Modified tannins AS _C -AS _P (cm ⁻¹)	Modified tannins BS _C -BS _P (cm ⁻¹)
3316 (vs, broad)	3373 (vs, broad)	3361 (vs, broad)
2926	2929	2922
1868 (w)	1909 (w)	1731 (m)
1618 (vs)	1613 (vs)	1617 (s)
1506 (ms)	1504 (ms)	1508 (m)
1454 (s)	1451 (s)	1454 (m)
1343 (m)	1342 (ms)	1345 (w)
1308 (mw)	1223 (m)	1157 (mw, broad)
1232 (w)	1177 (mw)	1040 (mw)
1200 (w)	1163 (mw)	845 (w)
1155 (mw)	1117 (mw)	803 (w)
1089 (m)	1029 (m)	771 (w)
1068 (m)	1008 (w)	689 (w)
1023 (s)	839 (m)	614 (w)
971 (w)	765 (w)	
842 (m)	699 (w)	
766 (w)	571 (m)	
728 (w)		
707 (w)		
623 (w)		

in a drum was performed in the following phases: (A) Washing: leather (100 g), water (200 g), Sinteral BD (0.5 g), Oxalic acid (0.5 g), *T*: 35°C, time 20 min. (B) Neutralization: leather (100 g), water (200 g), sodium formate (1 g), Intan 103 (3 g), *T*: 35°C, time 20 min. (C) Tanning: This process was carried out using the modified tannins or mimosa tannin. Each leather was divided in two parts and one side was tanned with one of the modified tannins while the other side was treated with mimosa tannin. A fat product was used as auxiliary substance. Leather

(100 g), water (50 g), polymer (10 g), Fat H50 (0.5 g), *T*: 30°C, time 60 min. (D) Dyeing and exhausting of the color: The process was performed in two steps. In the first step leather (100 g) was treated with water (50 g) and Brown CG color (3 g) at room temperature for 30 min than the leather (100 g) was treated with water (100 g), formic acid (1.5 g) at *T*: 50°C for 20 min. (E) Application of fat: This last process was performed using leather (100 g), water (150 g), Fat-H50 (5 g), *T*: 45°C; time 60 min.

At the end of the working process the leather was dried through suction under vacuum, then through hot cylinders.

Physical analysis of tanned leathers

The physical tests were carried out using the IUP (International union physical tests of leather)^{10,11} and IUF (International union fastness)¹³ procedures. The tests were performed on samples of leather collected and treated as reported by the IUP/2 and IUP/3 methodology.

1. Determination of the tensile strength and percentage elongation-IUP/6,
2. Determination of tear load-IUP/8,
3. Determination of distension and strength of grain by Ball Burst Test-IUP/9,
4. Determination of water resistance of flexible leather-IUP/10,
5. Determination of color fastness of leather to light: Xenon lamp-IUF/402.

The data of the physical analysis are reported in Table III.

TABLE III
Physical Tests on Leather Tanned with Modified Tannins

Tannin	Water absorption (%)	Tensile strength (N/mm)	Tear load (N/mm)	Strength of the grain (bar)	Light stability (Blue scale)
Mimosa	38.1	166.6	66.5	7	4.5
AS _P 1	65.8	195	67.8	10	4.0
AS _P 2	57.2	140	60.1	9	4.0
AS _P 3	55.2	131	57.5	8.5	4.0
AS _P 4	46.4	96.9	41.9	7.5	3.5
AS _C 1	60.1	210.3	70.3	20	7.0
AS _C 2	54.4	156.2	63.4	20	6.5
AS _C 3	51.4	144.1	60.1	20	6.0
AS _C 4	42.3	107.8	45.9	10	6.0
BS _P 1	65.5	171.5	58.8	10	5.0
BS _P 2	60.2	151.7	57.1	9	5.0
BS _P 3	51.4	126.6	56.3	8.5	5.0
BS _P 4	50.6	106.9	48.2	7.5	6.5
BS _C 1	56.2	135.4	60.2	15	6.5
BS _C 2	55.5	147.7	58	25	7.5
BS _C 3	50.1	159.2	50.2	30	7.0
BS _C 4	48	168.3	46.1	No breaking	7.0

TABLE IV
Leather Tanned with Mimosa and Modified Tannins—Sensorial Evaluation

Tannin	Grain	Color	Fluency	Reactivity	Fullness
Mimosa	+	+	+	+	+
AS _p 1	+++	+++	+++	+++	++
AS _p 2	++	-	++	n.d.	+++
AS _p 3	++	-	++	++	++
AS _p 4	---	--	-	-	-
AS _c 1	++	+++	+++	+++	++
AS _c 2	++	+	++	n.d.	+++
AS _c 3	++	-	++	++	++
AS _c 4	---	--	-	-	-
BS _p 1	++	+	++	++	++
BS _p 2	++	+	++	++	++
BS _p 3	++	+	+	+	++
BS _c 1	-	+	-	+	++
BS _c 2	+	+	++	++	++
BS _c 3	+	++	++	++	++
BS _c 4	+	++	+	+	++

(---) bad; (--) poor; (-) sufficient, (+) medium, (++) high, (++++) excellent.

Sensorial analysis of tanned leathers

The sensorial tests were performed by three referees and the media of their evaluations of grain, color, fluency, reactivity of the tanned leathers were reported in Table IV.

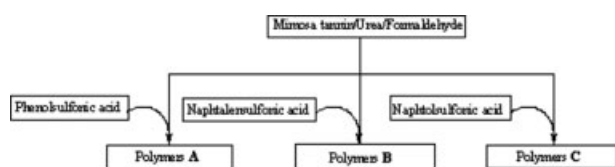
RESULTS AND DISCUSSION

Syntheses of modified tannins

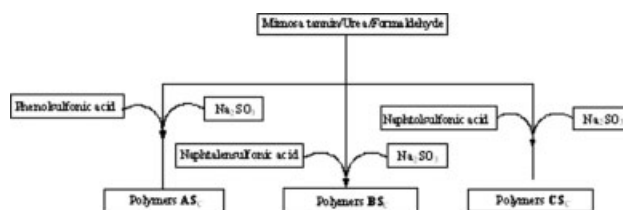
Tannins are largely studied and employed; however, their structures and the mechanism of their reactions with condensing agents such as formaldehyde and urea are not well clarified.

This lack of information is mainly due to the complex composition of natural extracts of tannins, to their different composition as a function of their provenience, and to the season of crop.

The modification of tannin with formaldehyde is usually employed to obtain an extensive amount of products usually employed as glues in the wood industries,^{14–25} in the production of flocculating agents,²⁶ to prepare ion-exchange resins,^{27–29} to tan leather,^{30,31} and so on.^{32,33} Numerous articles are known on the applications of these polymers, but very few studies are reported concerning the compo-



Scheme 1 Polymers of A–C series.



Scheme 2 Polymers of AS_C–CS_C series.

sition and structure of the products obtained. Model reaction may be used to rationalize the products formed such as those involving the synthesis of phenolic resins³⁴ or the polymerization of catechin,³⁵ that may be correlated with the polymerization of tannins with formaldehyde and urea.

The modified tannins usually have a low solubility in water while the products required for hide tanning must have a high solubility in water since they are employed in a water medium.

To obtain a polymer showing a high solubility in water, sulfonic acid was employed in the polymerization process.

Products

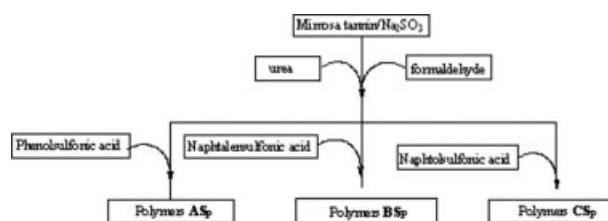
In this research, mimosa tannin has been polymerized with urea and formaldehyde, and a great attention has been paid to obtain products having a moderate increase of the molecular weight (the highest value does not exceed 5500 amu, Table I).

Three series of polymers were obtained and classified on the basis of the sulfonic acid employed (Scheme 1):

- polymers *A*, containing phenolsulfonic acid;
- polymers *B*, containing naphthalensulfonic acid;
- polymers *C*, containing naphtholsulfonic acid.

Several polymers with different properties have been obtained for each series using different reagents ratio.

The polymers of A–C series show a low solubility in water; therefore, a sulfiting agent was used to obtain new modified polymers. Three new series of polymers were obtained carrying out the sulfitation process in the same time of the polymerization (Scheme 2):



Scheme 3 Polymers of AS_p–CS_p series.

TABLE V
Physicochemical Properties of Modified Tannins

Polymer	Water solubility (%)	Viscosity (cst)*	Tanning substances (%)	Molecular weight (amu)*
Mimosa	98.0		70.0	1009
AS _{p1}	98.8	1.047	56.6	2276
AS _{p2}	98.5	1.063	62.2	2870
AS _{p3}	98.5	1.076	65.1	3341
AS _{p4}	94.0	1.101	22.3	5353
AS _{c1}	98.5	1.042	50.4	2042
AS _{c2}	98.5	1.055	60.1	2539
AS _{c3}	98.5	1.070	63.2	3238
AS _{c4}	93.0	1.093	19.2	5069
BS _{p1}	97.5	1.040	28.6	2011
BS _{p2}	97.5	1.048	30.1	2255
BS _{p3}	97.5	1.058	33.6	2920
BS _{p4}	96.5	1.068	37.5	3613
BS _{c1}	97.5	1.040	26.2	1955
BS _{c2}	97.5	1.048	30.4	2200
BS _{c3}	97.5	1.055	31.4	2876
BS _{c4}	96.5	1.063	36.2	3037

* A water solution containing 10 g/L was employed.

- polymers AS_c;
- polymers BS_c;
- polymers CS_c.

Alternatively, the sulfitation was carried out before the polymerization, obtaining three additional series of polymers (Scheme 3):

- polymers AS_p;
- polymers BS_p;
- polymers CS_p.

Synthesis of polymers

Reactions were usually carried out in acid medium, at a temperature of 85°C for 16 h, working with a water solution containing tannin, urea, formaldehyde, and sulfonic acid that acted also as catalyst (Table I). At the end of the reaction, water and volatile products were removed through distillation at reduced pressure, and the residue was analyzed and characterized (Tables II and V).

Polymers of A series. These products were obtained using mimosa tannin, formaldehyde, urea and phenolsulfonic acid. The acid employed was an industrial product containing the *para*-isomer as the main component. As a consequence, these products have a structure close to that reported in Figure 1. Three polymers were obtained using different tannin/formaldehyde molar ratio, while the amount of phenolsulfonic acid and the tannin/urea molar ratio was almost the same in all syntheses.

Polymers of B series. These compounds were prepared using mimosa tannin, urea, formaldehyde, and naphthalensulfonic acid. The acid was an industrial product containing a mixture of 1- and 2-naftphalensulfonic

acid. The polymerization usually involves the unsubstituted naphthyl ring.³⁶ Assuming that mimosa tannin reacts through the catechin moiety, a possible structure of the product is reported in Figure 2.

Three polymers were obtained using different molar ratios of tannin/formaldehyde, while the molar ratio of formaldehyde/urea and the molar ratio of naphthalensulfonic acid were kept constant in all synthesis.

Polymers of C series. These polymers were obtained using mimosa tannin, urea, formaldehyde, and naphtholsulfonic acid. The acid was an industrial product containing a mixture of 2,4- and 2,6-naphtholsulfonic acid. The acid may react through the 1,3-position, due to the orientating action of the oxydrilic group and the influence of the other ring on an electrophilic addition.³⁵ The products formed with 2,4-naphtholsulfonic acid are more difficult to hypothesize, due to the activating, *ortho/para* orientation of the oxydrilic group contrasted by its steric hindrance and the presence of the sulfonic group that affects the substitution on the adjacent aromatic ring. Assuming that tannin is involved in the reac-

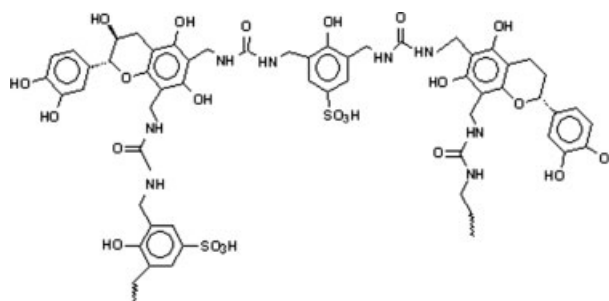


Figure 1 Schematic structure of the polymers of A series.

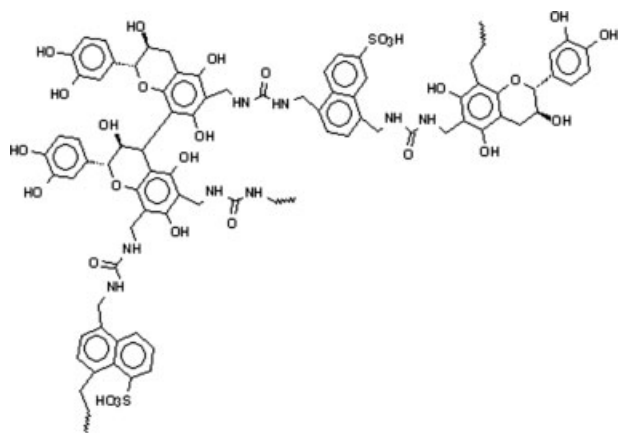


Figure 2 Schematic structure of the polymers of B series.

tion through the catechin group, a possible structure of polymers C is reported in Figure 3.

Two products were prepared, the first one (C1), with a tannin/formaldehyde molar ratio of 6.18 and, in consideration of its low solubility in water, a second product (C0) containing exclusively mimosa tannin and naphthalensulfonic acid.

Sulfitation: Polymers of AS, BS, CS series

Sulfitation is the industrial process usually carried out in the presence of sulfur dioxide, sodium sulfite, sodium thiosulfate,³⁷ or sulfuric acid with the aim to introduce a sulfonic group in the polymers, increasing their solubility in water. In this article the sulfitation with sodium sulfite has been carried out using soft reaction temperature and acidity than in the process with sulfuric acid. The concomitant effect of moderate temperature and reducing property of Na_2SO_3 has avoided, at least partially, the oxidation

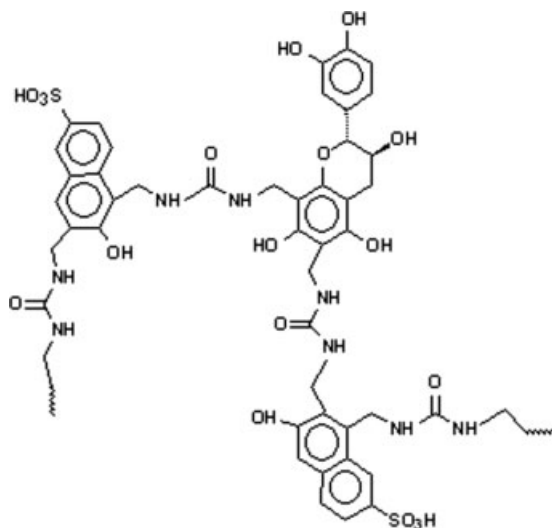


Figure 3 Schematic structure of the polymers of C series.

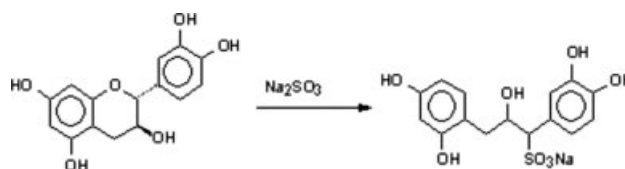


Figure 4 Sulfitation of catechin in its monomeric form.

of the hydroquinonic moiety of tannin. The reaction of Na_2SO_3 with tannin gives rise to two types of polymers. The first one is formed by reaction of the catechin group in its monomeric form by opening the pyranic ring³⁸ (Fig. 4), while the second is obtained through a reaction of the dimeric form of catechin giving a breaking of the interflavonoid ring in the C-4, C-6 (or C-8) position³⁹ (Fig. 5).

Sulfitation process. The sulfitation may be carried out before, during (tandem), or after the polymerization process. Among these options, the sulfitation carried out in a step subsequent to the polymerization has been ruled out due to the difficulty to perform a reaction on polymers having a low solubility in water.

Between the other two possibilities the sulfitation carried out in the course of the polymerization is more economic because less reaction time and energy for heating are required. Furthermore, in the tandem process a sulfomethylation reaction may take place. This last reaction, employed in the synthesis of synthetic tannins,⁴⁰ is carried out at medium temperature (80°C) using phenol, formaldehyde, and sodium sulfite, causing the insertion of a sulfomethyl group in the aromatic ring (Fig. 6).

Synthetic tannins obtained by this way have a better resistance to light degradation than sulfonated sintans prepared using the classic sulfonation process.

Because of the few information available on these products, the sulfitation procedure before and during the polymerization process has been investigated.

Sulfitated polymers. The solubility in water of sulfitated polymers is largely improved with respect to the polymers of the A–C series.

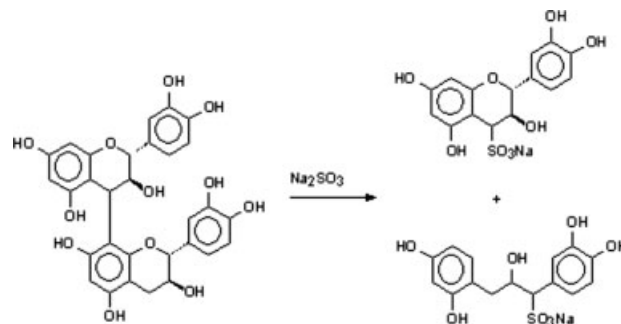


Figure 5 Sulfitation of catechin in its dimeric form.

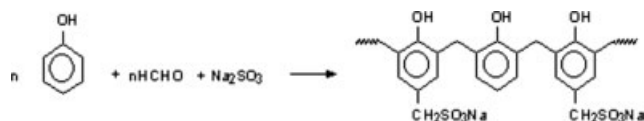


Figure 6 Sulfomethylation of phenol.

Taking into account the composition of these polymers, a possible structure of the products synthesized through a sulfitation carried out before the polymerization is similar to that reported in Figure 7 for the AS_P series.

When a tandem sulfitation-polymerization is carried out, some sulfomethyl groups may be inserted in the polymers, and a possible structure of the final products is similar to that reported in Figure 8 for AS_C polymers.

Analogous structures may be hypothesized for polymers of the BS and CS series.

Four series of polymers were prepared for each class of products (AS_P , AS_C , BS_P , BS_C , CS_P , and CS_C) differing for the tannin/formaldehyde molar ratio while the formaldehyde/urea molar ratio and the amount of sulfiting agent were almost constant (Table I). The sulfitation was carried out before polymerization at 85°C with a reaction time of 6 h then the polymerization was performed as reported earlier. In the tandem process, the sulfitation was carried out by adding the sulfitation agent together the crosslinking products and heating for 16 h at 85°C. At the end of the reaction, the water was removed at reduced pressure, and the modified tannins were analyzed and characterized.

Polymer characterization. Modified tannins were analyzed and characterized through physicochemical and technological tests. In Scheme 4 are reported the

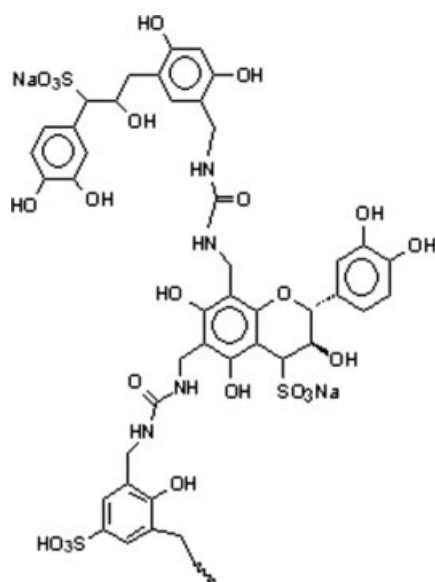


Figure 7 Schematic structure of polymers AS_P .

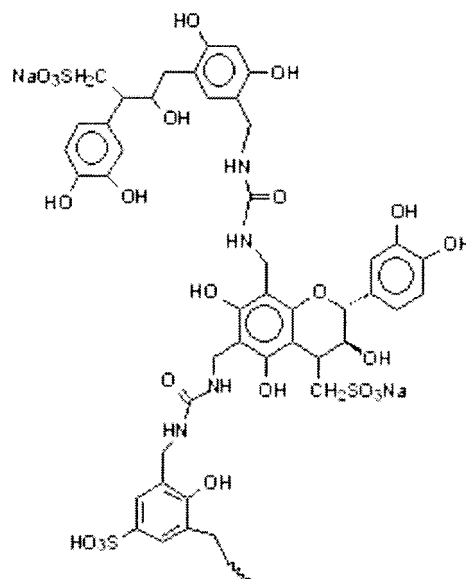


Figure 8 Schematic structure of polymers AS_C .

tests performed on the polymers and in Scheme 5 those carried out on leather tanned with modified tannins.

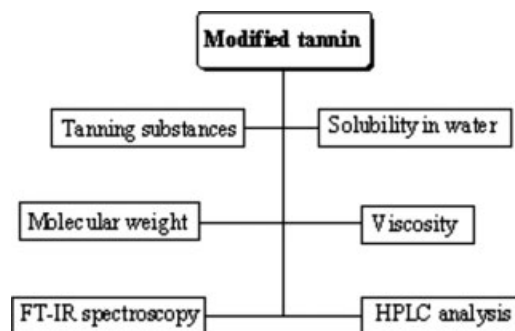
Solubility in water

The water solubility is the main characteristic required for polymers employed in the tanning of hide. As a consequence, the polymers having an insoluble residue higher than 7% have been discarded. The solubility was tested by following two procedures:

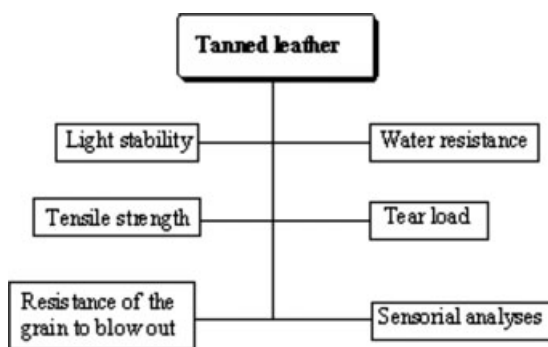
- Filtering method
- Centrifugation method

The procedures employed to carry out these methods are reported in the experimental part.

Polymers of A, B, C series. Polymers of **A** series show very low solubility also when a tannin/formaldehyde molar ratio of 6.12 is used, that means a very low amount of crosslinking agent. As a consequence,



Scheme 4 Tests performed on modified tannin.



Scheme 5 Tests performed on tanned leather.

these polymers show properties very close to those of natural tannin.

The water insolubility is increased in the polymers **B**, and therefore, these products can not be used as tanning agents. These results, even if foreseeable because naphthalensulfonic acid is employed to produce auxiliary sintans, indicate these polymers as very poor tanning agents.

The insolubility showed by polymers **A** and **B** is further enhanced in the polymers **C** ruling out these products as tanning agents even for research purpose. The insoluble residue of **C0** polymer, that is the product obtained by the reaction of tannin with naphtholsulfonic acid without crosslinking agents such as urea and formaldehyde, is 30%. These data suggest that additional reactions are involved during the polymerization (i.e., the crosslinking reaction between mimosa tannin and naphtholsulfonic acid).

Polymers of AS_P, AS_C, BS_P, BS_C series. Performing a sulfitation process before or, alternatively, in the course of the polymerization process, more soluble polymers were obtained. These polymers show an insoluble residue that remains constant in the first three polymers of each series while it improves in the fourth product when the tannin/formaldehyde molar ratio is lower than 1. However, the solubility in water is acceptable for all polymers because it is higher than 93% (Table V) and these polymers were tested as tanning agents. The polymers of the **BS_P** and **BS_C** series were obtained using a lower ratio of tannin/formaldehyde with respect to the corresponding polymers of the **AS_P** and **AS_C** series.

Sulfitated polymers of **C** series show a very low solubility even if they were obtained without formaldehyde and urea. As a consequence, the experiments on these polymers have been interrupted.

Tanning substances

Tanning or nontanning substances were evaluated using the method employed for tannin extracts. No direct method is described to evaluate tanning substances and in this article the methodology reported as "filter method" or "method of Procter" has been

adopted.⁴¹ This procedure is described in the experimental part.

Polymers of series A, B, C. The tanning substances present in polymer **A1**, having the highest solubility among this series is 69% almost the same value of mimosa extracts (70%), confirming the low difference between polymer **A1** and mimosa tannin.

The tanning substances of the other polymers of **A**, **B**, and **C** series were not evaluated in consideration of their low solubility in water.

Polymers of AS_P, AS_C, BS_P, and BS_C series. The amount of tanning substances in polymers of the **AS_P**, and **AS_C** series, Table V, is slightly lower, for the first three terms of each series, than the value obtained for mimosa tannin. This value increases with the increase of the amount of formaldehyde employed in the polymerization process, while there is decrease in the last terms of the same series (polymers **AS_{P4}** and **AS_{C4}**), having a very low amount of nontanning substances. In all the cases, the amount of tanning substances is higher in the polymers of the **AS_P** series than the corresponding terms of the **AS_C** series.

The polymers of the **BS_P** and **BS_C** series show lower tanning substances than in the polymers of the **AS_P** and **AS_C** series. These differences may be ascribed to the substitution of phenolsulfonic acid with naphthalensulfonic acid; that is an acid usually employed to obtain auxiliary sintans, and therefore used as dispersing agent more than as tanning product. In the polymers of each **BS_P** and **BS_C** series, the amount of tanning substances increases as the molar ratio of mimosa tannin/formaldehyde decreases, and the molecular weight of the polymer increases. Furthermore, the value of tanning substances slowly increases among all terms of each **BS** series. This behavior may be ascribed to the lower molecular weight of the last terms of these polymers than the polymers of the **AS_P** and **AS_C** series.

The tandem sulfitation/polymerization process gives polymers having a lower amount of tanning substances with respect to those obtained through sulfitation performed before the polymerization.

Viscosity

The viscosity of water solutions of these polymers was tested using a Cannon Fenske viscosimeter, (Table V) on the polymers of the **AS_P**, **AS_C**, **BS_P**, and **BS_C** series.

As expected, the viscosity increases as the amount of formaldehyde employed in the polymerization process increases, in agreement with polymers having an increasing molecular weight. The viscosity of the polymers in the different series follows the order: **AS_P** > **AS_C** > **BS_P** > **BS_C**. Higher viscosity is shown for the **AS_{P4}** polymer (Table V) connected with its high molecular weight. The **BS_C** and **BS_P**

polymers show a lower increase inside each series, than the **AS** polymers, in agreement with the lower ratio of mimosa tannin/formaldehyde used in the polymerization.

Molecular weight

The numerical average molecular weight (M_n) of the polymers has been evaluated without any preliminary separation or purification of the products obtained in the course of polymerization (precipitation, electro dialysis, extraction using the Craig apparatus¹²). An absolute method was employed using a vapor pressure osmometer on water solution of modified tannins (Table V).

Polymers AS_P, AS_C, BS_P, BS_C series. The molecular weight of these polymers is, as expected, in agreement with the viscosity data. The molecular weight increases as the molar ratio of mimosa tannin/formaldehyde used in the polymerization process decreases. For instance, in the **AS_P** polymers the M_n is 2276 amu for **AS_P1** and 3341 amu for **AS_P3**, and a larger increase is shown for **AS_P4** with a molecular weight of 5353 amu.

The molecular weight of the **AS_C** polymers is lower than that of the corresponding polymers of the **AS_P** series and the same trend is shown by the **BS** polymers. Among the **BS** polymers, the increase of the molecular weight is lower than that shown among the corresponding **AS** series in agreement with the low increase of the molar ratio of mimosa tannin/formaldehyde used in the polymerization process.

FTIR spectroscopy

The FTIR spectroscopy was employed to characterize the new polymers and to compare these products with mimosa tannin, employed as reference material. The main absorbances of the FTIR spectra are reported in Table II.

AS_P, AS_C, BS_P, BS_C polymers. The main difference in the FTIR spectra among the starting material and the synthesized polymers is observed in the fingerprint region, confirming that the functional groups present remain unaltered while modifications in the structure of the products are introduced. The FTIR spectra of polymers **AS_P** and **AS_C** show almost the same absorbances, confirming that polymers with similar groups and structure are obtained (Table II).

HPLC analysis

The HPLC analysis was employed to follow the polymerization reactions and to characterize the final products. It has been useful to collect qualitative results and to avoid complex procedure to identify the progress of the reactions. Several problems have been solved to define the procedure adopted because few data are reported on HPLC of tannin and their

reproducibility is not very good. These difficulties are attributed, by some authors, to the ability of tannins to complex the metal of chromatographic columns, and sometimes glass columns are suggested to avoid these problems.³⁷ In this article, a reproducible chromatographic procedure has been obtained by modifying a method reported for the analysis of tannins present in wine.⁴² HPLC analyses were carried out using a C18 column and a water/methanol solution acidified with perchloric acid up to a pH of 2.5 as eluent. The resolution of the chromatograms was not very good due to the complex composition of the products. Mimosa tannin is in fact a mixture of oligomeric products having a close structure, functional groups, and different molecular weights and therefore hard to separate. Changes in the number, form, and retention time of the HPLC peaks with respect to those present in the starting material has been detected. To confirm the validity of this method, a hydrolysable tannin (Mirabolano tannin) has been analyzed, obtaining reproducible analysis and well-separated peaks.

Polymers of AS_P, AS_C, BS_P, and BS_C series. The retention time and form of peaks have been correlated with those detected in the mimosa tannin chromatogram. The form of peaks in the range among 40 and 70 min changes regularly from a square form (in mimosa tannin and in the first terms of each series) to a triangular form in the last terms of these polymers (**AS_P3**, **AS_C3**). These changes in the form of peaks are attributed to the formation of products having a higher molecular weight: as a consequence, the dispersivity of the peaks is reduced and their forms change. HPLC analysis of the polymers **AS_P4** and **AS_C4**, in agreement with the previous analysis (molecular weight and viscosity) show a different chromatogram: several peaks disappeared and the form of the remaining peaks is flat.

The lower increase in the tannin/formaldehyde molar ratio used to obtain the **BS_P** and **BS_C** polymers may be noticed also by the HPLC chromatograms. The retention time of the peaks among 40 and 70 min is similar to that obtained with mimosa tannin while the form of the peaks changes from square to triangular as shown for the chromatograms of the first polymers of the **AS_P** and **AS_C** series.

Hide tanning with modified tannins: Efficiency of the synthesized polymers

Hide tanning has been considered as the most important characterization to evaluate the modified tannins. The new products were employed to perform tanning of hide using the following procedure.

The process has been performed on hide from 3-years old Rumanian cow, having a weight of 2–3 Kg of humid leather. The hide was previously submitted

to unhairing, neutralization, than each hide was divided in two parts, one side employed for the tanning process with the modified tannins and the other side was tanned with mimosa tannin as reference.^{10,11}

The tanning process in a "drum" has been carried out in the following phases: (A) Washing: It was carried out to clean the hide from dirty products deriving from previous treatment: transport, storage, unhairing, and so on. A tenso-active agent was employed in the bath containing oxalic acid, using a bath ratio (RB: ratio between water and hide)⁴³ of 200% at $T = 35^{\circ}\text{C}$. (B) Neutralization: It was performed to increase the pH, avoiding in the course of the subsequent tanning process, a high absorption of tanning substances. This process was carried out using sodium formate, an auxiliary agent (Intan 103), RB = 200% and $T = 35^{\circ}\text{C}$. (C) Tanning: This process was the applicative test of the modified tannin synthesized. It was carried out using the synthesized polymers and mimosa tannin as reference product. Each pelt was divided in two sides, one tanned with one of the modified tannins while the other side was tanned with mimosa tannin. A fat product (Fat H50) was used as auxiliary substance, using an RB = 50% and $T = 30^{\circ}\text{C}$. (D) Dyeing and exhausting of the color: All leathers tanned were taken together and submitted to a dyeing process using an acid dye. Using an acid dye, the pH of the bath is kept lower than the isoelectric point of the proteins of leather. The proteins will be positively charged and their affinity to the dye improved. The acidity was not kept high avoiding a very high affinity of the dye with proteins and a hard diffusion of the dye inside the dermis and a heterogeneous dispersion. In a subsequent step the pH was lowered increasing the affinity of the leather with the dye and exhausting the dye itself present in the bath. The RB was 50%, $T = 30^{\circ}\text{C}$ during the dyeing and RB = 100% and $T = 50^{\circ}\text{C}$ in the exhausting step, employing formic acid to reduce the pH in the second step. (E) Greasing: This last process was performed to improve the elasticity of the finished leather using a $T = 45^{\circ}\text{C}$ and an RB = 150%; The ALPA H 50 product was employed as fat product.

At the end of the tanning process the leather was first dried by suction under vacuum, then using hot cylinder.

The properties of tanned leathers were subsequently evaluated through physicochemical and sensorial tests as reported in the following paragraphs.

Tests on tanned leather

The physicochemical (technological) and sensorial tests on tanned leather (Scheme 5) have been performed according to the IUP (International union of physical tests of leather)^{10,11} and IUF (International union fastness)¹³ tests using samples collected and conditioned according to prescriptions of IUP/2 and

IUP/3. The tests performed are reported in Scheme 5 and their results in Tables III and IV.

Water resistance of flexible leather-IUP/10. Polymers of *A, B, C series*: The results obtained on the characterization of these polymers and therefore the properties of these modified tannins have been confirmed by tests on leather tanned with modified tannins **A1** and **B1**. Leathers show poor properties of the sensorial analyses: scarcely fullness, low flexibility and low elasticity, low exhausting of color and a reduced reactivity.

Polymers of **AS_P**, **AS_C**, **BS_P**, **BS_C** series: The dynamic permeability of leather tanned with modified tannins shows a value of water absorbance that decreases as increases the molar ratio tannin/formaldehyde employed in the syntheses of polymers. The values of the last terms of each series show a lower water absorbance than the leather tanned with mimosa tannin. Leathers obtained using **AS_C** and **BS_C** products, that is products obtained through a tandem process, show a low water absorbance with respect to the leather obtained using **AS_P** and **BS_P** polymers (Table III).

Tensile strength and percentage elongation-IUP/6. Polymers **AS_P**, **AS_C**, **BS_P**, **BS_C**: Tensile strength of leather tanned with modified tannins of the **AS_P**, **AS_C**, **BS_P** series decreases as increases the molecular weight of the polymers. The leather tanned with the first terms of each modified tannins series shows tensile strength better than the leather treated with mimosa tannin. Just using the second term of each series the tensile strength of the leather tanned with polymers is almost the same of that obtained with leather tanned with mimosa tannin (Table III).

A different behavior is shown by leather tanned with polymers **BS_C**. The tensile strength improves by improving the molecular weight of the polymer up to the **BS_{C4}** product. Only this last polymer gives leather having almost the same resistance than leather tanned with mimosa tannin. These results may be explained by interactions among the polymers, the fat and the leather. Only in this case a fundamental role may be played by the fat agent used in the retanning process improving the tensile strength of the leather (Table III).

Tear load-IUP/8. The tear load of leather tanned with polymers of the **AS_P**, **AS_C**, **BS_P**, **BS_C** series decreases as the molecular weight of the polymers increases. The tear load of the leather tanned with the first term of the series **AS_P**, **AS_C**, **BS_P**, is better than that of leather tanned with mimosa (Table III).

All leathers tanned with polymers obtained through a tandem polymerization/sulfitation process (**AS_C** and **BS_C** series) have values of tear load better than those of the leather obtained using the **AS_P** or **BS_P** polymers. Samples tanned with **BS_P** and **BS_C** polymers show values of tear load lower than those obtained with **AS_P** and **AS_C** polymers (Table III).

Distension and strength of grain by ball burst test-IUP/9. The distension and strength of the grain of leather tanned with **AS_P**, **AS_C**, **BS_P**, **BS_C** polymers are always good and better than the value obtained with leather tanned with mimosa tannin. Among each series of the polymers tested, the value decreases as the molecular weight of the polymers increases (Table III). On the contrary samples of leather treated with **BS_C** polymers give a reverse trend. In fact the value of distension and strength of grain increases with molecular weight of the polymers and no breaking is obtained using the **BS_C4** polymer (it was impossible to detect a blow out using the available apparatus). In our opinion this good result is not connected with the "fat process" as happen for the data of "tensile strength." The data obtained support the hypothesis of a different interaction among leather and polymers **BS_C** with respect to the other polymers tested (Table III).

Color fastness to light: Xenon lamp-IUF/402. Leathers tanned with modified and mimosa tannins were submitted to the same dyeing process and its light stability was evaluated using the IUF/402 method. The results are reported in Table III.

Polymers AS_P, AS_C, BS_P, and BS_C series: The samples of leather tanned with modified tannins of the **AS_P** and **BS_P** series do not show a good stability to light giving, in some cases, values lower than those obtained using leather tanned with mimosa tannin. The value inside each series remains almost constant. Better results are obtained with leather tanned with **AS_C** and **BS_C** polymers: These modified tannins give leather having a good light resistance, better than that obtained using leather tanned with mimosa. This behavior may be explained assuming the formation of sulfomethylic moieties during the tandem polymerization. These groups have a high stability to light as happen when auxiliary sintans are employed.

Sensorial tests

These tests concern with some particular sensation that the leather touched may transmit to an operator. It is obvious that this evaluation depends by the sensibility and experience of the operator and it is at least in part subjective. However if these analyses are carried out by different skilled evaluators the reproducibility may be good. The tanned leather was submitted to the evaluation of three operators and the results obtained were in good agreement (Table IV). The results have been expressed through different shading such as fine and close grain, color shining, firmness, reactivity and elasticity of the leather. The results are compared with those obtained with leather tanned with mimosa tannin.

Leathers tanned with **AS_P** polymers generally showed a good quality, in particular when the **AS_P1**

polymer was employed. Poor results were obtained using **AS_P4** polymer.

Leathers tanned with **AS_C** polymers showed a behavior similar to that shown by leathers tanned with **AS_P** polymers but better sensorial performances than using polymers **AS_P** were obtained. Good results were found using polymers **AS_C1** while decreasing quality was shown with **AS_C2** > **AS_C3** and **AS_C4** polymers.

These data may be explained assuming that the last terms of the **AS_P** and **AS_C** series do not show a deep penetration of modified tannin inside the leather but, due to their higher molecular weight, remain on the surface. This behavior suggest the use of these polymers as pretanning agents where the main goal is the treatment of the leather surface while the penetrating action is reserved to the product employed in the tanning process.

Leather treated with **BS_P** and **BS_C** polymers showed a scarce penetration and intensity of the color. The other sensorial properties usually decrease as the molecular weight of the polymer increases following the trends shown by the **AS_C** and **AS_P** polymers, even if less evident.

CONCLUSIONS

Leather tanned with modified tannins (polymers **AS_C**, **AS_P**, **BS_C** and **BS_P**) show good technological and sensorial properties. A controlled increase of the molecular weight of the polymers improves the quality of these tanning agents giving leathers having better quality than those obtained with mimosa tannin. The first term of the **AS_P** and **AS_C** series (molecular weight around 2,000 amu) give good tanned leather: A good increase of the distension and strength of grain, tensile strength and tear load has been evidenced. These technological properties are associated with good sensorial properties: the leather shows a fine grain, good elasticity, reactivity, and fullness. These results may be explained with a good penetration and diffusion inside the dermis structure of the polymers having a suitable molecular weight. If the molecular weight is too higher the tanning agents remain on the surface or do not interact with hide. On the basis of these considerations the low amount of tanning substance present in polymers **AS_P4** and **AS_C4**, where the molecular weight of the product is an obstacle to a deep penetration inside the leather, has been explained. This hypothesis is supported by microscopic observation of a cross view of the leather showing the polymer on the surface. Moreover, we must note that when the product having a high molecular weight is able to partially penetrate and diffuse inside the leather it causes a stiffening of dermis with loss of elasticity. Such behavior may be assumed for leathers treated with polymers **AS_P3**,

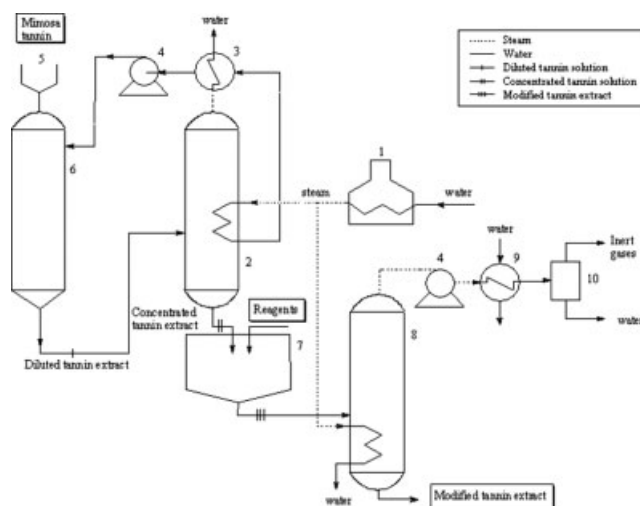


Figure 9 A schematic draw of the process to obtain modified tannins: (1) oven for steam production; (2) distillator; (3) condenser; (4) pump; (5) mimosa supply; (6) mimosa dissolutor; (7) polymerization reactor; (8) distillator; (9) condenser; (10) phase separator.

AS_{C3}, BS_{p3}, BS_{p4}, BS_{C3}, BS_{C4}. These polymers gave tanned leather quite fullness but with a low elasticity.

In conclusion, the modified tannins, especially those of the **AS** series having a low increase of the molecular weight, are found to be better tanning agents than mimosa tannin. An important result has been obtained concerning the color fastness of leather to light. The high stability is evident especially with leather tanned with polymers **AS_C**, where a sulfomethylic group is present.

These results are very interesting because the modified tannins may be synthesized through a slightly modification of the process used to obtain the extract of mimosa tannin. It is only required, in a tannin extraction process, the insertion of a polymerization reactor after the extractor and before the last concentration unity (Fig. 9).

The polymers of the **BS** series show poor quality as tanning agents but interesting properties as pre-tanning products where a deep diffusion of the products inside the dermis is not required.

References

- Heidemann, E. In *Leather in Ullmann's Encyclopedia of Industrial Chemistry*; Elvers, B., Hawkins, S., Schulz, G., Ed.; VCH: Weinheim, 1990; Vol. A15, p 259.
- Covington, A. D. *Chem Soc Rev* 1997, 26, 111.
- D'Aquino, A.; Barbani, N.; D'Elia, G.; Lupinacci, D.; Naviglio, B.; Seggiani, M.; Tomaselli, M.; Vitolo, S. *J Soc Leather Technol Chem* 2004, 88, 47.
- D'Aquino, A.; D'Elia, G.; Naviglio, B.; Seggiani, M.; Tomaselli, M.; Vitolo, S. *J Soc Leather Technol Chem* 2003, 87, 189.
- Vitolo, S.; Seggiani, M.; D'Aquino, A.; Barbani, N.; Naviglio, B.; Tomaselli, M. *J Am Leather Chem Assoc* 2003, 98, 123.
- Simon, C.; Pizzi, A. *J Appl Polym Sci* 2003, 88, 1889.

- Simon, C.; Pizzi, A. *J Am Leather Assoc* 2003, 98, 83.
- Simon, C.; Pizzi, A. *J Am Leather Assoc* 2003, 98, 193.
- George, B.; Pizzi, A.; Simon, C.; Triboulot, M. C. *J Am Leather Assoc* 2004, 99, 1.
- International Union of Leather Technologists and Chemists Society (IULTCS). <http://www.iultcs.org/home.asp>.
- Simoncini, A.; De Simone, G.; Fiore, U. *Metodi Internazionali per l'analisi fisica dei cuoi (IUP)*, Stazione Sperimentale per l'industria delle pelli e delle materie concianti; Turin, Italy, 1982.
- Manzo, G. *Chimica e tecnologia del cuoio*, Media Service, Legnano; Milan, Italy, 1998.
- Simoncini, A.; Del Pezzo, L.; Manzo, G. *Metodi Internazionali per l'analisi fisica dei cuoi (IUC) e per le prove di resistenza dei cuoi tinti (IUF)*, Stazione Sperimentale per l'industria delle pelli e delle materie concianti; Turin, Italy, 1982.
- Pizzi, A. *J Appl Polym Sci* 1979, 23, 1901.
- Pizzi, A. *J Appl Polym Sci* 1979, 23, 1889.
- Pizzi, A.; Roux, D. G. *J Appl Polym Sci* 1978, 22, 2717.
- Goulding, T. M.; Pizzi, S. A. *Afr. Pat.* 801,583 (1980), Can. 95:1,88,380.
- Lopez-Suevos, F.; Riedl, B.; Gomez de Marzoa, R. L. *J Adhesion Sci Technol* 2003, 17, 1507.
- Jung, B.; Roffael, E. *Adhesion* 1989, 33, 28.
- Yang, W. *Faming Zhuanli Shenqing Gongkai Shuomingshu* Can. 143:134,394 (2003).
- Trosa, A. *Eur. Pat. Appl.* 924280(1999), Can. 131:32,737.
- Pizzi, A.; Sorfa, P. H. *Olzforschung Holzverwertung* 1979, 31, 113, Can. 92:59,851.
- Pizzi, A. *J Appl Polym Sci* 1979, 23, 2777.
- Pizzi, A.; Scharfetter, H. O. *J Appl Polym Sci* 1978, 22, 1745.
- Pizzi, A. *J Appl Polym Sci* 1979, 24, 1257.
- Luck, E.; von R. Lipinski, G. W. In *Food Additives in Ullmann's Encyclopedia of Industrial Chemistry*; Elvers, B., Hawkins, S., Schulz, G., Ed.; VCH: Weinheim, 1990; Vol. A11, p 576.
- Miranda, C. E. S.; Olivares, S.; Reis, B. F.; Luzardo, F. M. *J Braz Chem Soc* 2000, 11, 44.
- Chen, J. C.; Chen, F.; Walterick, G. C. *U.S. Pat.* 5,684,109 (1997), Can. 131:45,253.
- Oliveira, I.; Cruz, V.; Visconte, L.; Dezotti, M. In *Proceedings of the International Symposium on Natural Polymers and Composites*, 4th ed.; Sao Pedro, Brazil, 2002, p 392.
- Roy, B. *Indian Pat.* 93825, Can. 70:12,696 (1966).
- Wollenberg, H. G. *Ger. Offen.* 2,042,757 (1971), Can. 75: 22,540.
- Pena, C.; Larranaga, M.; Gabilondo, N.; Tejado, A.; Echeverria, J. M.; Mondragon, I. *J Appl Polym Sci* 2006, 100, 4412.
- Kikuchi, K.; Miyake, K.; Takatsuji, I.; Nakai, T.; Tokuda, M. *Jpn. Pat.* 74-141349 (1976), Can. 85:110,370.
- Ciardelli, F.; Crescenzi, V.; Pezzin, G.; Peggion, E. *Macromolecole, scienza e tecnologia*, Pacini ed.; Pisa, 1986.
- Kiatgrajai, P.; Wellons, J. D.; Gollob, L.; White, J. D. *J Org Chem* 1982, 47, 2913.
- Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon: Boston, 1985.
- Hemingway, R. W.; Karchesy, J. J. *Chemistry and Significance of Condensed Tannins*; Plenum Press: New York, 1988.
- Sears, K. D. *J Org Chem* 1972, 37, 3546.
- Foo, L. Y.; McGraw, G. W.; Hamingway, R. *J Chem Soc Chem Commun* 1983, 672.
- Hayashi, H.; Oka, S. *Bull Instrum Chem Res Kyoto Univ* 1974, 52, 514, Can. 82:124,965.
- Bravo, G. A. *Chimica Analitica per l'Industria del Cuoio*, Associazione Italiana fra i Fabbrianti di estratti tannici, "Italtannino"; Milan, Italy, 1952.
- Salagoity-Auguste, M.; Bertrand, A. *J Sci Food Agric* 1984, 35, 1241.
- In a tanning process in a "drum" it is useful to define the bath ratio (RB) as the ratio between the water (weight) and the humid leather employed.