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COMMON TORMENTIL TANNINS AS TANNING MATERIAL FOR LEATHER PROCESSING

У роботі представлені результати дослідження властивостей танідів, отриманих з кореня перстачу прямостоячого (Potentilla erecta) і властивості ними видублених шкір. Визначено, що ці таніди відрізняються високою спорідненістю до колагену. Шкіра, видублена цими танідами відрізнялася коричнюватим забарвленням, лицьовою поверхнею без стяжки, високою міцністю при розтягуванні й низьким відносним видовженням. Температура зварювання шкір досягала 73 °С.

Ключові слова: *забарвлення, активні барвники, спорідненість*

Hides can be tanned using chromium, titanium, aluminium and zirconium salts, aldehydes, isocyanates, synthetic and vegetable tannins, or combining these materials. All tanning methods have advantages and disadvantages, but as yet many decades the chromium tanning prevails as mostly cheap and simple method for producing of various sorts of leather. On the other hand, this method leads to a formation of hazardous waste, and, also, finished product (leather) after exploitation becomes unwelcoming waste by environmental point of view. All mentioned force to pursue the new tanning methods and the new tanning materials.

An opinion exists, that best alternative to chroming is tanning with synthetic and vegetable tannins [1, 2, 3]. By the way, the tanning by vegetable tannins is one of the oldest tanning methods. Tanned with tannins leather is less thermo stable than chromed but it less swells in water and can be dyed using direct dyes [4]. Products from the leather tanned with tannins perfectly keep form [5]. An extract of every plant dyes the leather by colour which is typical only for that extract. This is the reason why the tanned by tannins leather is used for the particular fashionable articles.

The tannins can be extracted from wood and bark of quebracho, oak, chestnut, willow etc, and, also, from roots and fruits of some plants. The tannins volume depends on resources of raw materials, which becomes decreased every year, accordingly, tannins production decreases year in, year out [6] (from 420000 tones in 1950 year down to 180000 tones in 1990 year). Search and investigation for new raw materials for the tannins extraction goes on to date. Nowadays, possibilities to use for leather tanning a rootstock of rhubarb, red mangrove (*Rhizophora racimosa*), bagaruwa (*Acacia nilotica*) are investigated [7].

Talking of plants, which grow in Lithuania, the Common tormentil (CT) characterizes by high content of tannins. This perennial plant is permeated in Europe forest zones, West Siberia, Caucasus. Cultivated CT is used for plant of green areas. The highest content of tannins is accumulated in CT (*Potentilla erecta*) rootstock: 14–31%. These tannins contain of condensed (most) and hydrolysed (minority) tannins. Also the rootstock of CT contains of triterpene saponins, quinic acid. Additionally, there are flavonoids, ellagic acid, phlobaphenes, wax, resin, starch. The CT rootstock characterises by bactericidal, antiphlogistic**,** stopping haemorrhage action, wherefore is used in medicine [8].

Materials and methods

Salted cattle hide was used as a raw material. The samples for the investigation had been taken from the lower part of the hide, which was cut into pieces10x20cm, and a series for experiments formed from these pieces. A half of the hide samples till vegetable tanning were processed according to conventional technology of sole leather processing. Second half of the pieces were processed in the same method but without bating process. Accordingly, the vegetable tanning was executed after the bating or directly after deliming omitting pickling.

Amount of non-washable materials was determined using hide powder prepared under method described in literature [9]. Moisture content in the hide powder was 12.7%, amount of total nitrogen 18.1%, and pH of the hide powder was 6 – 7.

Dry CT rootstock powder, containing of 26.13% tannins, 10.42% of water, 51.8% of matter soluble in water and 14.6% of matter non-soluble in water, was used for the preparation of the tannins extract. The extract of tannins was obtained as followed: on 100g of CT rootstock powder was poured 1 litre of boiled water and stored in thermostat for 4 hours at 70^{o}C. Produced extract was evaporated on water bath till a formation of viscous mass. Extract in such form was used for investigation of its properties and tanning as well.

Also, for were used organic tanning materials: *Indusol ATO, Ormotan C and Blancotan W* (producer "Silva", Argentine). *Indusol ATO:* soluble extract of quebracho containing of 74–75% tannins. *Ormotan C*: a modified vegetable extract containing of 70–72% tannins. Synthan *Blankotan W* is a product of phenol polycondensation containing of 71–73% tanning materials.

Affinity of tannin extract to hide was determined according to Grossman and Bender method [10]. Solutions of extract with concentration of tannins 4g/l were used. PH of the solutions was 4.5. For the investigation different amount of the hide powder was taken: 2, 5, 7, 9 and 15 g. Every portion of the hide powder was chromed, washed, and 100 ml of tannins solution was poured. The samples prepared in such way were shaken with agitation 40–50 rpm during 30 minutes. After the hide powder treatment with tanning materials the tanning solutions were filtered through dry linen textile, and, further, through filtering paper covered with kaolin. After the filtration the filtrate must be transparent. Amount of dry materials in the initial solution and in the filtrate was determined and a difference calculated. The difference corresponds to amount of tannins absorbed by the hide powder. Shrinkage temperature, pH, chemical and strength properties of leather were determined according to methods described in literature and standards [9, 11, 12, 13].

The main aim of research was to investigate a tanning ability of CT tannins and properties of leather tanned by CT tannins.

Results and discussion

Properties of CT tannins extract. Firstly the constituents of CT tannins extract were determined. It was established that the extract contains of 32.25% tannins, 56.51% soluble (non tannins) and 11.24% insoluble in water in water materials.

Very important property is the affinity of tannins to hide. It is related with the ability of tannin to be absorbed in the structure of collagen. So, the absorption of tannins by hide powder was investigated. Soluble extract of quebracho *Indusol ATO* and modified vegetable extract *Ormotan C* were used for the comparison. Results of the absorption dependence on the sort of tannins are presented in Fig. 1.

Under chosen conditions of experiment, the amount of tannins in the treatment solution was 0.4g. Herewith, it was established that hide powder have absorbed even 0.77g of materials from CT extract.

It is markedly bigger amount than after treatment with *Indusol ATO or Ormotan C*. So, it means that using CT extract the hide powder absorbs not only tannins but also other materials, which present in the extract. By the way, the amount of materials absorbed by hide powder exceeded amount of tannins in all cases of treatment. Consequently, the absorption both tannins and non-tannins goes on when tanning.

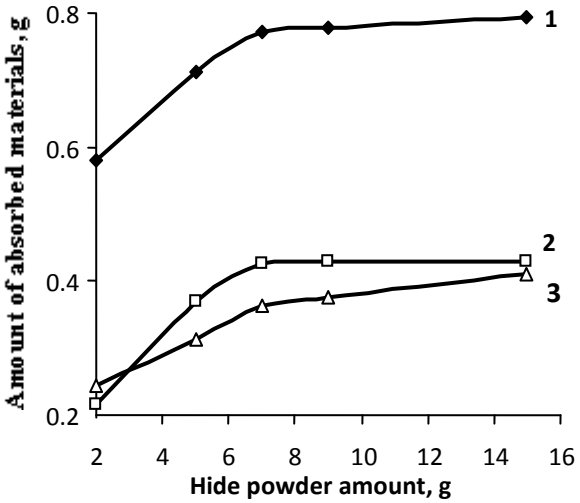

Fig 1. **Dependence of obsorbed tannins amount on used for treatment amount of hide powder: *1* – CT tannins extract; *2* – Indusol ATO; *3* – Ormotan C.**

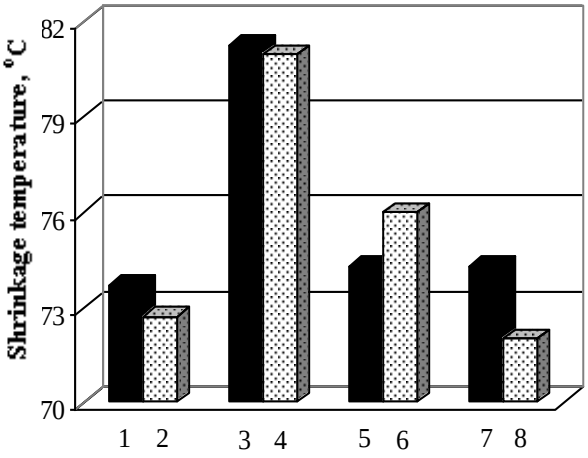

Fig 2. **Leather shrinkage temperature after tanning when hide before tanning is non-bated (*1, 3, 5, 7*) or bated (*2, 4, 6, 8*): *1,2* – CT tannins extract; *3,4* – Indusol ATO; *5,6* – Ormotan C; *7,8* – Blancotan W.**

It should be noted, that in cases of tanning with the CT extract or *Indusol ATO* the amount of absorbed materials increases increasing amount of used hide powder up to 7g. Further increasing of the hide powder amount does not lead to observable change of the absorbed materials content. So, the hide powder absorbs tannins from CT and quebracho extracts (*Indusol ATO)* lightly and completely. Because of sorption dynamic in both cases is similar, it can be proposed that those extracts are similar from the absorption rate viewpoint. Since the one of most important properties, which decide popularity of tannins extracts (quebracho for sample), is a property to penetrate fast into derma [4], authors propose that CT extract also characterizes by such property.

When is used the modified vegetable extract *Ormotan C*, the content of absorbed materials increases increasing the amount of the hide powder. Consequently, the absorption of such tannins is more complicated comparing with both tannins of CT and quebracho. To absorb all tannins, which present in modified extract, is needed even 15 g of the hide powder. The obtained results allow proposition that tannins of CT are absorbed fast and such extract can be used for tanning of leather.

Tanning process investigation. To estimate tanning properties of CT tannins extract and to compare these tannins with other used in leather manufacture tannins, the investigation of the tanning process and the tanning indexes was carried out.

The tanning conditions were: H_2O 110 % (% from unhaired hide mass), tannins or synthans 20%, initial pH of the tanning solution 5.9–6, duration 48 h, run continuously.

Dependently on what properties the processed leather should to have, the tanning with tannins or synthans can be carried out for both hides bated and not bated. It was the reason why firstly the tanning of not bated hide pieces executed.

For the tanning were used: CT tannins extract, soluble extract of quebracho *Indusol ATO*, modified vegetable tannins extract *Ormotan C* and synthan *Blancotan W*. All tanning materials were dissolved in water having temperature 50°C. PH of the tanning solutions was adjusted to 5.9–6.0 adding 10% Na_2SO_3 solution. PH of pelt before tanning was 7.23.

The rate of tannins diffusion into hide and of joining with collagen in great part depends on the medium pH. Due to this, the pH of the tanning solution was determined periodically during all process. In the end of the tanning, amount of the matter, which presented in solutions, was established and exhaustion calculated (Table 1).

Table 1. **pH of tanning solutions and exhaustion of tanning materials**

Index	Tanning material			
	CT extract	*Indusol ATO*	*Ormotan C*	*Blankotan W*
Actual pH of tanning solution	4.90	4.63	4.23	4.32
Tanning solution pH:				
after 24 h of tanning	6.2	6.3	5.9	6.3
after 48 h of tanning	6.0	6.2	5.6	6.3
Exhaustion of tanning materials, %	89.8	88.6	84.9	79.1

The solution of CT tannins, like the solutions of the other tannins, is acidic. Its pH is 4.9. For a deceleration of joining with derma and for an acceleration of the tannins penetration, the pH of CT tannins was increased up to 5.9. The change of the pH of the CT tannins solution, like of the other tannins solution used, was negligible during tanning process. So, in all tanning cases the conditions of process were close. Most part of tanning materials pass into hide tanned using the CT extract: 89.8 %.

This figure confirms results presented in Fig. 1 and the proposition that CT tannins characterize by high affinity to collagen.

After tanning the tanned leathers were treated as follows:

Washing: H_2O 200% (% here and further from limed hide mass), run continuously;

Fatliquoring:H_2O 100%, temperature 60°C, *Lipoderm Licker SLW* 10%, duration 1 h, HCOOH (100%) 1.5 %, duration 15 min, HCOOH (100%) 1.5%, duration 15 min, all process run continuously;

Washing: H_2O 200%, temperature 40°C, duration 30 min, run continuously;

Drying at temperature 20-22°C, duration 24 h.

Chemical and strength tests were carried out for the dry samples.

Chemical composition of the samples obtained after tanning with various tannins is presented in Table 2, the strength properties presented in Table 3.

Results show that the chemical composition of leather obtained from non-bated hide differs from chemical composition of leather obtained from bated hide. Herewith, leather produced after bating characterized by lower content of matter soluble in dichloromethane.

Table 2. **Chemical composition of tanned leather obtained from non-bated/bated hide**

Component, % from absolutely dry mass	Tanning material			
	CT extract	*Indusol ATO*	*Ormotan C*	*Blankotan W*
Water	10.85/11.01	10.84/9.98	10.95/10.25	10.16/11.17
Proteins	50.0/56.46	46.17/52.12	47.91/53.23	52.38/62.81
Matter soluble in dichloromethane	10.90/7.09	9.50/7.49	12.28/8.67	12.97/6.22
Matter washable by H_2O	3.21/6.63	3.84/6.63	4.58/7.26	5.85/8.46
Inorganic matter non-washable by H_20	0.54/0.44	0.43/0.59	0.42/0.57	0.41/0.58
Tanning matter non-washable by H_2O	24.50/18.37	29.22/23.19	20.02/23.86	18.23/10.76

Unfortunately, literature review did not reveal data about the influence of the bating on the diffusion of vegetable tannins into derma. It is known only that thinner structural elements of derma are available for chromium compounds comparing with tannins [14]. Also it is known [15] that during bating, due to the removal of non-collagen proteins, the structural elements become closer. On the other hand a bating increases the of hide air permeability [16]. Summarising can be proposed that the bating leads to formation of opened but having lesser diameter than in non-bated hide pores.

Since the molecules of tannins are comparatively large, the penetration of them through smaller pores is complicated. Due to this, the tannins after the penetration into outer layers of hide “plug up” these layers, and this stops further diffusion of the tannins. This supposition is confirmed by the established amount of washable matter, which commonly contains of polysaccharides, inorganic salts, simple organic acids and other materials having smaller molecules than tannins. It is seen (Table 2) that leather obtained from the bated hides absorbs more mentioned materials comparing with non-bated one. The reason is that when the tannins do not pass into derma, the “empty space” is filled by washable by water materials.

Table 3. **Strength properties of tanned leather obtained from non-bated/bated hide**

Index	Tanning material			
	CT extract	*Indusol ATO*	*Ormotan C*	*Blankotan W*
Tensile strength, N/mm^2	15.5/12.3	13.3/13/1	16.2/15.5	12.8/12.2
Relative elongation when the strain of 10 N/mm^2 is reached, %	43/52	70/54	60/44	69/39

The tensile strength of leather was in a range 12.2-16.2 N/mm^2. Leather produced by the tanning with the CT tannins characterized by comparatively high tensile strength and lowest percentage extension. The percentage extension of tanned by the CT tannins leather was higher when the bating process was carried out. It lets proposition that the CT tannins do not distinguish by properties of plasticizers. So, when the derma absorbed less the CT tannins it became more plastic comparing with the leather having more tannins. By the way, the lesser amount of tannins in the leather decreased tensile strength of the leather. Hence, the CT tannins impart higher tensile strength, and, herewith, decrease the plasticity of leather. Shrinkage temperature determination results are presented in Fig. 2.

Simon and Pizzi reports [2] that after tanning with several tannins shrinkage temperature of leather reaches only 61-65^{o}C. The results of our investigation show that tanning with CT tannins of non-bated hide allows reaching sufficiently high shrinkage temperature (73.6^{o}C). This value is only negligible lower than after tanning with *Ormotan C* or *Blancotan W*. The highest shrinkage temperature is reached when tanning wit quebracho tannins (*Indusol ATO*), which characterizes by good tanning properties.

The bating leads to the lower shrinkage temperature after the tanning comparing with the non-bated samples. Exception is the tanning with modified vegetable tannins *Ormotan C.*

Here the most important thing is the tanning matter non-washable by H_2O. In cases of tanning with CT tannins, *Indusol ATO* or *Blankotan W* the amount of mentioned matter is decreased accordingly 7.47, 6.13 and 6.03% comparing with non-bated samples. Only in the case of tanning with *Ormotan C* the amount of the tanning matter non-washable by H_2O is increased in bated samples. So, such situation decides the determined values of leather shrinkage temperature.

The leather samples tanned with CT tannins distinguished by brownish grain colour, grain was not shrunk but they were markedly stiffer than other samples.

Conclusions

Common tormentil (*Potentilla erecta*) rootstock is rich by tannins. It contains of 32% tannins. Absorption of the tormentil tannins by hide powder is fast and exhaustions of tannins reaches 90%. Such indexes allow supposition that tormentil tannins have high affinity to collagen. Leather tanned with tormentil tannins has high tensile strength but low relative elongation, what shows that these tannins do not distinguish by properties of plasticizers. Shrinkage temperature of leather tanned with tormentil tannins reaches 73.6^{o}C, and it is almost same like after tanning with modified vegetable tannins or synthans. The bating process before tanning disimproves joining of tannins, the strength properties and the shrinkage temperature of the tanned leather, when the tormentil tannins are used for tanning.

Leather tanned with Common tormentil tannins distinguished by brownish grain colour, its grain was not shrunk but the leather was markedly stiffer than leather tanned with other tanning materials.

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Танниды Лапчатки прямостоячей как дубящий материал для производства кож

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В работе представлены результаты исследования свойств таннидов, полученных из корней Лапчатки прямостоячей (*Potentilla erecta*), и свойства ими выдубленных кож. Определено, что эти танниды отличаются высоким сродством к коллагену. Кожа, выдубленная этими таннидами, отличалась коричневатой окраской, лицевой поверхностью без стяжки, высокой стойкостью при растяжении и малым относительным удлинением. Температура сваривания кож достигала 73 ^{o}C.

Ключевые слова: окраски, активные красители, родство.

Common tormentil tannins as tanning material for leather processing

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Presented research devoted for investigation of Common tormentil (Potentilla erecta) tannins properties and tanning peculiarities. It was established that tormentil tannins have high affinity to collagen. Leather tanned with tormentil tannins distinguished by brownish grain colour, grain was not shrunk, and it had high tensile strength but low relative elongation. Shrinkage temperature of leather tanned with tormentil tannins reaches 73.6^{o}C, and it is almost same like after tannins with modified vegetable tannins or synthans.

Keywords: staining, active dyes, affinity.