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## RECOVERING VALUES FROM VEGETABLE TANNED LEATHER

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This invention relates to a process for preparing certain amino acids, tannins and tannin acids. It is directed particularly to the recovery of these values from vegetable tanned leather scrap or waste. At the present time scrap vegetable tanned leather has very little value. On the other hand, there is no inexpensive commercial source for these amino acids. The present invention, therefore, is one for obtaining valuable materials from substantially useless by-products which are produced in quantity in the shoe and leather fabricating industries.

Vegetable tanned leather is essentially a combination of hide substance of animal origin, and tanning agents of vegetable origin. The hide substance is a protein called collagen which is composed of a group of compounds known as amino acids in their simplest form. The tanning agents in vegetable tanned leather, which are described herein as tannin and tannin acids, are composed mainly of glucosides of certain polyhydroxyphenolic acids derived largely from gallic acid and protocatechuic acid. In accordance with the present invention amino acids are derived from the collagen or hide substance and the tannins, tannin acids or tanning agents are obtained from the tanning agents present in the leather.

Briefly, this invention is based, first, upon the concept and determination that the collagen component and the tannin component of vegetable tanned scrap leather respond differently to hydrolyzing agents such as sodium hydroxide; and, second, that the products resulting from hydrolyzation of vegetable tanned scrap leather possess different solubilities in certain solvents whereby they readily may be separated one from another by extraction methods. Although collagen and tannin are both known to be hydrolyzable it has now been found that a difference exists in the ease with which the hide substance is hydrolyzed by alkalies in comparison with the tanning agents; the hide substance is resolved into simple amino acids more readily than the tanning agents are decomposed into simple polyhydroxyphenolic acids. In accordance with this invention hydrolysis of the scrap leather is conducted whereby the hide substance is substantially completely resolved into its amino acid component with a minimum effect upon or modification of the vegetable tanning agents that are present in the leather.

As a result of this differential hydrolysis, it has been determined that whatever hydrolytic products of the tannins that are formed, as well as the undecomposed tannins, are combined with the hydrolyzing agent to render them insoluble in certain organic solvents in which the amino acids, combined with the same hydrolyzing agent, are substantially soluble. For instance, in the employment of sodium hydroxide as the hydro-

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lyzing agent, the sodium compounds of the tannins and tannin acids are insoluble in the alcohol as a selective solvent, while the sodium compounds of the amino acids dissolve readily in the alcohol. This solubility behavior is anomalous in view of the fact that the tannins and their polyhydroxyphenolic acids are normally alcohol soluble. Moreover, the solubility behavior of the sodium salts of the amino acids from vegetable tanned leather also is unexpected inasmuch as the amino acids are not appreciably soluble in alcohol.

Sodium hydroxide is the preferred hydrolyzing agent in the practice of this invention because of its low cost and its ready solubility in water. However, other alkalies such as potassium hydroxide or the like may be employed in place of it. Ethyl alcohol is preferred as the selective solvent in the process because of its low boiling characteristics and the selective solubility which it exhibits for the products of hydrolysis. However, methyl alcohol or other low boiling alcohols and similar solvents or mixtures thereof may be employed.

A typical example of the process is as follows: 400 parts by weight of vegetable tanned leather, preferably shredded or finely comminuted, and 1000 parts by weight of aqueous sodium hydroxide solution of 15% to 25% concentration by weight are placed in a container which is equipped with a lid so that it may be tightly closed. During hydrolysis air should be excluded as the tannins and tannin acids oxidize readily in alkaline solution. The leather and the lye solution are heated to a temperature of approximately 80° C. to 100° C. from four to ten hours. During this treatment the leather is dissolved upon hydrolysis of the hide substance and a brownish-black liquor results which may form a soft gel upon cooling. The conditions of time, temperature and concentration of the alkali may be varied to yield a maximum hydrolysis of the hide substance and a minimum hydrolysis of the tanning agent. Hydrolysis is accelerated with an increase in heat and also with an increase in the concentration of the lye solution. Pressure also may be employed if desirable to accelerate the hydrolysis.

The mixture is now permitted to cool and approximately 3000 parts of ethyl alcohol by volume per each 1000 parts of hydrolysate mixture are added thereto and the mixture is then agitated, preferably out of contact with the air, for a short period of time to insure thorough mixing. Upon standing twelve to twenty-four hours two layers separate, one being a supernatant liquid and the other being a viscous brownish to black residue. The supernatant liquor may readily be decanted from the viscous residue.

The supernatant liquor or alcoholic extract contains the sodium salts of the amino acids and

is substantially free from the sodium salts of tannin and tannin acids. From this extract the alcohol may be recovered for reuse by distillation, leaving the sodium salts of the amino acids. These include particularly the sodium salts of glycine, alanine, proline and hydroxyproline. The sodium salts of other amino acids that may be present in appreciable amounts are aspartic acids, glutamic acid, leucine, serine and the like. Although arginine and lysine are hydrolytic products of collagen, the alkali hydrolysis may cause partial or complete dismutation of these. Some ammonia and amines are also liberated in the hydrolysis.

The black residue which is left after the alcoholic extract has been removed comprises the sodium compounds of the tanning agents originally present in the leather which will be found to have suffered a minimum of decomposition. This black residue first may be washed with alcohol if it is desired to free it of any amino acids which may be present. It may also be neutralized by acids such as sulphuric acid supplemented with sulphur dioxide, if desirable.

The sodium sulphate formed in this treatment is permitted to crystallize from the residue whereupon the resulting brown liquid will be found to possess tanning properties and may be used in the preparation of new vegetable tanned leather. This brown liquor containing the sodium compounds of the tannins and the tannin acids also may be heated or fused at higher temperatures with or without additional alkali to completely hydrolyze the tannins and tannin acids to gallic and protocatechuic acids from which pyrogallol and pyrocatechol, respectively, may be prepared. Accordingly, either the tanning agents or the polyhydroxyphenolic acids may be recovered which enables the process to be practiced according to which of the final products is most in demand. Moreover, the solution of the sodium salts of the amino acids may be used as a source for the individual acids or the solution may be treated with alkaline oxidizing agents directly by methods heretofore described, whereby the prolines are converted into pyrrole,

Vegetable tanned leather contains appreciable quantities of glucose and magnesium sulphate. These constituents are removed from finely comminuted leather if such removal is desired, by preliminary washing of the scrap with water. If the tannins and tannin acids are intended to be used as tanning agents then preliminary removal of the magnesium sulphate and the glucose enables a more concentrated tanning extract to be prepared.

Having described my invention, I claim:

1. The method of obtaining useful values from vegetable tanned leather, which method comprises subjecting said leather when it is in a comminuted form to differential hydrolysis in alkaline solution with exclusion of air to substantially completely hydrolyze the hide substance of the leather with a minimum effect on the tanning agents in the leather, and then, by means of a lower alcohol selectively extracting the products resulting from hydrolysis of the hide substance from the tanning matter and its derivatives.

2. A process for the preparation of amino acids and tannins and tannin acids from vegetable tanned leather, which process comprises subjecting the leather to differential hydrolysis in alkaline solution with exclusion of air and thereby substantially hydrolyzing the hide substance of the leather with minimum hydrolyza-

tion of the tannins and tannin acids, and then separating the amino acids resulting from hydrolysis of the hide substance from the tannins and tannin acids by selective solvent extraction with a lower alcohol.

3. A process for recovering useful values from vegetable tanned leather, which method comprises effecting hydrolysis of the hide substance of the leather with minimum effect on the tannins and tannin acids present therein by subjecting the scrap leather in substantial absence of air to differential hydrolysis in aqueous alkaline solution, then subjecting the hydrolysate to selective solvent extraction with a lower alcohol as solvent in which the alkali compounds of the hydrolyzed hide substance are soluble in preference to the alkali compounds of the tannins and tannin acids.

4. A process for recovering amino acids and tannins and tannin acids from vegetable tanned leather, which comprises subjecting said leather to hydrolysis by an aqueous alkaline solution, in the absence of air then separating the amino acid salts resulting from hydrolysis of the leather hide substance from the alkali compounds of the tannins and tannin acids by means of a low boiling alcohol.

5. A process for recovering amino acids and tannins and tannin acids from vegetable tanned leather, which comprises subjecting said leather in the absence of air to hydrolysis by an aqueous alkaline solution, then separating the amino acid salts resulting from hydrolysis of the leather hide substance from the alkali compounds of the tannins and tannin acid by means of ethyl alcohol.

6. The process for the recovery of amino acids and tannins and tannin acids from vegetable tanned leather, which process comprises subjecting said leather to hydrolysis by an aqueous solution of sodium hydroxide, with the exclusion of air, and separating the sodium salts of the amino acids resulting from hydrolyzation of the hide substance of the leather from the sodium compounds of the tannins and tannin acids by means of a low boiling alcohol.

7. The process for the recovery of amino acids and tannins and tannin acids from vegetable tanned leather, which process comprises subjecting said leather to hydrolysis by an aqueous solution of sodium hydroxide, with the exclusion of air, and separating the sodium salts of the amino acids resulting from hydrolyzation of the hide substance of the leather from the sodium compounds of the tannins and tannin acids by means of ethyl alcohol.

8. A process for recovering amino acids and tannins and tannin acids from vegetable tanned leather, which process comprises treating said leather with an aqueous alkaline solution, controlled as to time and temperature, and in the absence of air, to effect hydrolysis of the hide substance of the leather to amino acids with a minimum effect on the tannins and tannin acids present in the leather, and then recovering the amino acids formed through hydrolyzation from the tannins and tannin acids by extraction with a low boiling alcohol in which the amino acids are soluble.

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#### REFERENCES CITED

The following references are of record in the file of this patent:

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