UNITED STATES PATENT OFFICE.

WILLIAM M. NORRIS, OF PRINCETON, NEW JERSEY.

ART OF TAWING OR TANNING HIDES OR SKINS.

SPECIFICATION forming part of Letters Patent No. 588,874, dated August 24, 1897.

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To all whom it may concern:

Be it known that I, WILLIAM M. NORRIS, a citizen of the United States, and a resident of Princeton, Mercer county, New Jersey, have invented certain Improvements in the Art of Tawing or Tanning Hides or Skins, of which the following is a specification.

The invention relates particularly to that method of tawing or tanning leather now being largely practiced and known as "chrome" tanning; and the object of the invention is to attain greater economy and other advantages, hereinafter particularly pointed out, in the practice of said method.

The "beamwork" of my improved process is substantially the same as the beamwork in chrome tannage as at present ordinarily practiced, and the tanning is substantially the same, with the exception that in my improved process I provide for a continuous evolution of nascent hydrogen in the second or reducing bath. This nascent hydrogen operates to change the thiosulfuric acid or the sulfurous acid present or liberated in said bath into hyposulfurous acid, which is a more powerful reducing agent and possesses other advantages, hereinafter referred to.

By the term "hyposulfurous acid" as used in this description I mean not the compound which has been some time so called, and which is otherwise and more properly known as "thiosulfuric acid," but the compound expressed by the symbol H_2SO_2 or $H_2S_2O_4$, and known also as "hydrosulfurous acid."

I first tan or taw the hides or skins by subjecting them, as heretofore practiced, to bichromate of potash or analogous salt, such as bichromate of soda, dissolved in water, to which an acid, such as hydrochloric acid, is added, taking, say, for each one hundred pounds of raw hides or skins about five pounds of bichromate of potash or its equivalent and two and one-half pounds of hydrochloric acid of 21° Baumé or an equivalent amount of sulfuric acid, the amount of water in the bath being sufficient to properly cover the skins. The hides or skins having been left in this bath until thoroughly impregnated with the chromium compound are then removed, pressed, or "struck out" to remove surplus liquor, when the stock is ready for the reducing-bath.

So far my improved process does not depart from the process of chrome tanning as now ordinarily practiced; but in the present practice of chrome tanning, as known to me, the second or reducing bath consists, ordinarily, of hyposulfite of soda, by which I mean the compound $Na_2S_2O_3$, more correctly designated as "sodium thiosulfate," and hydrochloric acid in water. The thiosulfuric acid liberated by the action of the hydrochloric acid upon the hyposulfite of soda in this ordinary reducing-bath is very unstable and is resolved almost as rapidly as generated into sulfurous acid and sulfur, this action being so quick and energetic as to be easily observable. The active agent, therefore, in this bath is sulfurous acid, with which the hides or skins become impregnated, while sulfur is thickly deposited in the fibers on the grain and flesh sides of the hides or skins. To free the latter from the sulfurous acid and sulfur requires a thorough washing, which usually takes considerable time and requires the use of a number of reels or other apparatus, which might be otherwise more advantageously utilized, consumes, furthermore, much water, and is sometimes injurious to the leather. To overcome these objections to the now commonly employed reducing-bath, I add to said bath metallic zinc, whereby there is continuously liberated in the bath nascent hydrogen, which operates to convert sulfurous acid, when formed, into hyposulfurous acid, (the reaction being expressed by the equation

$$2H_2SO_3+H_2=H_2S_2O_4+2H_2O,$$

or, as it is stated in other books on chemistry,

$$H_2SO_3+H_2=H_2SO_2+H_2O,)$$

and, doubtless, it operates also to lessen or prevent the formation of sulfurous acid by converting the thiosulfuric acid produced by the action of the hydrochloric acid upon the hyposulfite of soda directly into hyposulfurous acid.

The method which I prefer for the development or liberation of the nascent hydrogen

is the very simple and economical method of placing a number of pieces of metallic zinc in the vessel containing the bath, these pieces being, where a reel is employed, sufficiently large and heavy to remain at the bottom of the bath without being disturbed by the motions of the liquor caused by the paddles in the reel. The bath being acid, a continuous liberation of nascent hydrogen from the metallic zinc will take place, but I wish it understood that I do not confine myself to this particular method of evolving nascent hydrogen in the bath, as other modes may be employed.

I have found the following to be an efficient reducing-bath made in accordance with my invention, although it will be understood that the proportions specified may be departed from without departing from the invention. For the treatment of, say, one thousand pounds of skins, a bath of one hundred and twenty-five pounds of hyposulfite of soda and fifty pounds of muriatic acid in six hundred and fifty gallons of water is prepared, and to this bath is added sixty pounds of metallic zinc. The zinc should be allowed to remain when the liquor is drawn off after the bath is exhausted and a new bath is prepared and about five pounds of metallic zinc should be added about once a week.

Instead of having pieces of zinc at the bottom of the reel the latter may be lined with sheet-zinc, thus exposing a large surface to the action of the acid solution.

Some manufacturers for their reducing or second bath use instead of hyposulfite of soda and acid a solution of what is commercially known as "bisulfite of soda" prepared for this purpose. This I understand to be an aqueous solution of sulfite of soda saturated with sulfurous-acid gas, and the bath may be the same as before given except that the acid is omitted and the hyposulfite of soda is replaced by an equal number of pounds of the bisulfite solution. In this case the zinc is used in substantially the same way as formerly described in connection with the reducing-bath of hyposulfite of soda and muriatic acid. Although no sulfur is developed in such a solution, the liberation of nascent hydrogen in such a bath would convert the sulfurous acid into hyposulfurous acid, which would be an advantage, and much less bisulfite would be required. Hence my invention is applicable to a bath of this character and is so claimed.

Nascent hydrogen acting upon a solution of bisulfite of soda gives rise to the reactions which are expressed by these equations:

$$4NaHSO_3+H_2=H_2S_2O_4+2Na_2SO_3+2H_2O,$$

or

$$2NaHSO_3+H_2=H_2SO_2+Na_2SO_3+H_2O.$$

It is customary after skins are taken from the first or chrome bath and struck out to dip them each singly into a dilute solution of hyposulfite of soda, to which muriatic acid is added, this treatment being for the purpose of bringing the stock into the best condition for the reducing-bath and for effecting a slight surface reduction, which acts to prevent the washing out of the chromium compound from the stock when placed in the reducing-bath.

A zinc-lined vessel may be advantageously used to contain the solution into which the stock is thus dipped, or pieces of zinc may be added to the solution, as the nascent hydrogen which will thus be developed will increase the efficacy of the solution, less hyposulfite of soda will be required, and less sulfur will be developed.

The results of my improvement are:

First. A comparatively small amount of sulfur is liberated and little or no sulfurous acid brought into contact with the skins or hides, so that when the latter are taken from the reducing-bath very little washing is necessary to perfectly cleanse them and make them quite neutral and in good condition for the subsequent finishing operations, and in this way material economies of time, labor, and apparatus are gained.

Second. Hyposulfurous acid being a much more powerful reducing agent than sulfurous acid, the quantity of hyposulfite of soda requisite for the reducing-bath is by my improvement materially reduced. About one-half of the quantity of hyposulfite of soda heretofore considered necessary will in my improved process suffice—that is to say, where twenty per cent. of the weight of the skins of hyposulfite of soda and five per cent. of the weight of the skins of muriatic acid have been used heretofore ten per cent. of hyposulfite of soda and five per cent. of muriatic acid will be sufficient when my improved process is employed.

Having thus described my invention, I claim and desire to secure by Letters Patent—

1. The process herein described of tawing hides or skins, said process consisting in subjecting the hides or skins to the action of a bath prepared from a metallic salt, such as bichromate of potash, then removing the hides or skins from said bath, and then subjecting them to the action of hyposulfurous acid, generated in and below the surface of a second bath, whereby it is immediately brought into direct contact with the hides or skins, substantially as specified.

2. The within-described process of tawing hides or skins, said process consisting in subjecting the hides or skins to the action of a bath prepared from a metallic salt such as bichromate of potash, and then to the action of a bath capable of evolving sulfurous acid, said bath having presented to it metallic zinc, substantially as specified.

3. The within-described process for tawing hides or skins, said process consisting in subjecting the hides or skins to the action of a

bath prepared from a metallic salt, such as bichromate of potash, and then to the action of a bath capable of evolving hyposulfurous acid, such as a solution of thiosulfate of sodium, the so-called "hyposulfite of soda" ($N_2S_2O_3$) in presence of an acid, such as hydrochloric acid, and metallic zinc, substantially as specified.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

WILLIAM M. NORRIS.

Witnesses:
CHAS. H. BANNARD,
WILL. A. BARR.