UNITED STATES PATENT OFFICE.

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SOLUTION FOR TANNING HIDES, PELTS, OR OTHER ANIMAL TISSUES.

SPECIFICATION forming part of Letters Patent No. 714,433, dated November 25, 1902.

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To all whom it may concern:

Be it known that I, OTTO PAUL AMEND, a citizen of the United States, residing in the city, county, and State of New York, have invented certain new and useful Solutions for Tanning Skins, Pelts, or other Animal Tissues, of which the following is a specification.

The history of the art of tanning is so well known by those skilled in its application that it is unnecessary to give the details thereof. It may be stated in a general way, however, that at the present time practically only two methods of tanning are employed. One of these is the well-known process in which organic extracts containing tannin are used, and the other is that known as "mineral tannage." It is to the latter that my invention relates.

The method of tanning by means of metallic salts—such as the salts of chromium and iron, for instance—has been known for many years; but such processes are more or less complicated and require a skilled chemist in order to produce good results, while the necessary step of "puring," in addition to weakening the structure of the skin, also requires constant care and attention to prevent destruction of the skin by climatic changes, such as rises in temperature and electrical disturbances. The leather produced by these processes leaves much to be desired in regard to quality, and the time required for the tanning operation is very considerable.

I have discovered that many of the defects inherent in tanning by means of mineral salts are obviated by the employment of a tanning liquor or solution which contains a nitrite of a leather-forming metal, and that the time required for the tanning of a skin or hide is thereby very materially shortened. Thus leather tanned in my solutions is superior to that produced by other known metallic processes in that it has a more porous or open texture, owing to less contraction during tanning, and this facilitates the washing out or freeing by any well-known means of any acid which it may contain, while the grain is left in a much better condition for subsequent manipulation or treatment than when produced by the other processes at present employed. Again, I have found that the time for tanning a hide is so much shortened by using my solutions that an ordinary sheep, goat, or calf skin, which requires immersion from sixteen to eighteen hours in a solution of a basic metallic salt, such as basic sulfate of chromium, or a basic chlorid or acetate of chromium, in order to be tanned can be tanned in my solution in about one hour, while heavy hides or pelts, such as those of steers, can be effectively tanned by an immersion of, say, twenty-four hours. Still again, by using my solutions the operation of puring may be entirely dispensed with, and "degreasing" is so far rendered unnecessary that a hide just as it is taken from the animal after being fleshed and washed may be effectively tanned in my solutions. If depilation is not desired, liming and "bating" are also dispensed with and the skin can be thoroughly tanned with the hair in place, while if the hair is to be removed liming and bating may be performed either before or after the skin has been tanned in my solutions. If the skin is to be depilated, and consequently limed, I prefer to remove the lime chemically by washing in a weak solution of acid, such as muriatic or acetic acid.

In preparing my solutions of a nitrite of a leather-forming metal I dissolve a salt of one of the leather-forming metals—chromium, iron, and aluminium in water at ordinary temperatures—and also dissolve a soluble nitrite of an alkali metal, such as nitrite of sodium or nitrite of barium, in water at ordinary temperatures, and then mix the two solutions to form my tanning solutions. In some cases there will be an insoluble precipitate formed, together with a solution of a nitrite of the leather-forming metal contained in the metallic salt, while in other cases no precipitate will be formed, but a partial decomposition takes place with the formation of a nitrite of the leather-forming metal in the solution. In the former instance the precipitate may be removed by filtration or decantation, as is well understood, while in both cases it is the solution containing the nitrite of the leather-forming metal that furnishes the tanning agent.

As illustrations of the first class of solutions I dissolve seven hundred and seventeen (the molecular weight) grams of crystalline chromic sulfate, $Cr_2(SO_4)_3+18(H_2O)$, in about

seven thousand grams of water at ordinary temperatures. I also dissolve six hundred and eighty seven (three times the molecular weight) grams of barium nitrite, $Ba(NO_2)_2$, in about seven thousand grams of water at ordinary temperatures. I then mix the solutions and remove the insoluble precipitate. The clear solution will contain nitrite of chromium and is the tanning liquor to be used.

Again, I dissolve three hundred and seventy-four (the molecular weight) grams of chromic oxalate, $Cr_2(C_2O_4)_3$, in about four thousand grams of water at ordinary temperatures. I also dissolve three hundred and sixty-nine (three times the molecular weight) grams of calcium nitrite, $Ca(NO_2)_2$, in about four thousand grams of water. I then mix the two solutions and remove the precipitate. The clear solution will contain nitrite of chromium and is the tanning liquor to be used. Of course the salts may be mechanically mixed first and then dissolved in water. I have found that four ounces of chromium nitrite to every gallon of water form an efficient and cheap tanning solution. When, however, the chlorids, acetates, formates, or nitrites of the metals are used with the nitrite of an alkali metal or of an alkaline earth no precipitate may be formed, but partial decomposition takes place, forming a metallic nitrite in the solution.

I have also found by experiment that I can form an efficient and cheap tanning solution by the use of chrome-alum, $K_2Cr_2(SO_4)_4+24(H_2O,)$ as follows: I dissolve chrome-alum in, say, ten parts of water at ordinary temperatures, and add to this solution a solution of sodium nitrite, $Na(NO_2,)$ in, say, ten parts of water at ordinary temperatures, the proportion of the chrome-alum to sodium nitrite being one molecule of the former to six molecules of the latter. The mixture of the two solutions in proportions of one part of the former to one part of the latter will form the tanning liquor. There will be no precipitate formed in this solution, but there will be a decomposition with the formation of nitrite of chromium in the solution.

Although I have specified chromium as a leather-forming metal in all of the foregoing, and I prefer to use it, I do not confine myself to the use of salts of this metal, but my invention includes the use of the salts of the other leather-forming metals—iron and aluminium. Thus in using a salt of aluminium I take, for instance, one part of aluminium-alum and dissolve it in, say, ten parts of water at ordinary temperatures, and add to this solution a solution of sodium nitrite $Na(NO_2,)$ in, say, ten parts of water at ordinary temperatures, the proportion of aluminium-alum to sodium nitrite being one molecule of the former to six molecules of the latter. The mixture of the two solutions in proportions of one part of the former to one part of the latter will form the tanning liquor which may be used in this strength or as a stock solution to be diluted with water if weaker solutions are desired. Again, if an iron salt is to be used I take, for example, ferric sulfate and dissolve one part in, say, ten parts of water at ordinary temperatures, and add to this solution of sodium nitrite $Na(NO_2)$ in, say, ten parts of water at ordinary temperatures, the proportion of ferric sulfate to sodium nitrite being one molecule of the former to six molecules of the latter. A mixture of the two solutions in proportions of one part of the former to one part of the latter will form the tanning liquor, which may either be used in this strength or as a stock solution which can be diluted with water if weaker solutions are desired. Nor do I confine myself to the use of the specific nitrites of the alkali metals named, but include the use of any soluble nitrite of an alkali metal or of an alkaline earth. Neither do I confine myself to the proportions of water specifically given, because it is obvious that the proportions of water may be varied according to the character of the hides to be tanned and the consequent strength of the liquor desired. The stated proportions in the illustrative examples are efficient for a rapid tanning of an ordinary sheepskin, while a slower tanning may be effected with a weaker solution. Again, with heavier skins, such as those of steers, a stronger solution may be used and tanning may be effected in from eighteen to twenty hours. I may state that I have used effectively, on one hand, a mixed solution of the two salts each dissolved in seven parts of water, and, on the other hand, a mixed solution of the two salts each dissolved in ninety-nine parts of water. From this it will be understood that the original solutions may be used directly for tanning purposes or as stock solutions, which may be diluted with water, according to the strength of the tanning liquor desired.

In practicing my invention with chrome-alum, for instance, I take for every one pound of chrome-alum one half-pound of nitrite of sodium and dissolve the salts in water in proportions of from one part of the mixed salts to eight parts of water up to one part of the mixed salts to eighty parts of water, according to the strength of the solution desired. I then immerse in this solution the undepilated skin or pelt which has been previously washed and fleshed, but which has not been "pured." (Of course it can be pured if desired.) The effectiveness of the tanning in chrome tannage may be determined by the ordinary test of cutting off a piece of a skin in the bath and immersing it in boiling water. If the skin does not shrink, it has been converted into leather. So, also, the other ordinary tests are applied in the case of the other metals.

If depilation is desired, the skin may be limed, depilated, and bated before immersing it in the tanning-bath, or it may be limed, depilated, and bated after being tanned. If

the skin is bated, I prefer chemical bating by dissolving the lime in a weak solution of an acid, such as muriatic or acetic acid.

The same process and corresponding stœchiometrical proportions of salts should be used with the other salts of the different leather-forming metals and the nitrites of the alkali metals or of the alkaline earths, so as to form a nitrite of the leather-forming metal.

Thus for tanning with chromic sulfate and barium nitrite I take for every one pound of chromic sulfate one pound of barium nitrite and dissolve the salts in water in proportions of from one part of the mixed salts to eight parts of water, according to the strength of the solution desired, and so on for the other salts of the different leather-forming metals.

Of course my invention contemplates and comprises all methods of introducing into the bath or generating within the bath a nitrite of a leather-forming metal.

I do not in the present application claim the process of tanning which forms a part of my present invention, as such claims constitute the subject-matter of a divisional application filed April 18, 1902, Serial No. 103,580.

Having thus described my invention, what I claim is—

1. A tanning liquor consisting of an aqueous solution containing a salt of a leather-forming metal and a soluble nitrite of an alkali metal, or of an alkaline earth.

2. A tanning liquor containing chromium nitrite in an aqueous solution.

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Witnesses:
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