

UNITED STATES PATENT OFFICE.

GEORGE W. ADLER, OF PHILADELPHIA, PENNSYLVANIA.

PROCESS OF TAWING SKINS.

SPECIFICATION forming part of Letters Patent No. 638,685, dated December 12, 1899.

Application filed August 17, 1897. Serial No. 648,565. (No specimens.)

To all whom it may concern:

Be it known that I, GEORGE W. ADLER, a citizen of the United States, residing in the city of Philadelphia, State of Pennsylvania, have invented certain new and useful Improvements in Processes of Tawing Skins with Aluminium Compounds, of which the following is a full, clear, and exact specification.

My invention relates to the insoluble tawing by means of aluminium salts and chromic oxids of hides and skins that have been prepared for tanning by any usual beam-house treatment; and it consists of the process and composition hereinafter described, whereby the oxids or basic salts of aluminium and of chromium are separated out of their compounds in the presence of the skin and insolubly combined successively with the tissues of the skin resulting in the production of an insolubly-tawed skin which partakes of the nature of both alum-tawed leather and chrome-tawed leather in that it possesses the appearance, touch, fine grain, and softness characteristic of and peculiar to the former, while it has also the perfectly insoluble nature which distinguishes the latter.

The essential features of my process consist in a preliminary treatment of the skin, composed of three consecutive steps or acts—viz., first, tawing the skin-tissues with an aqueous solution of aluminium sulfate and sulfate or chlorid of sodium, preferably the chlorid, then giving fixation to the same by means of an aqueous solution of hyposulfite of soda, as heretofore practiced in the art, and finally reapplying to the skin thus treated a solution in lesser quantity than at first of the ingredients first applied—viz., aluminium sulfate and a sodium salt. A thoroughly-tawed skin is thereby produced which is insoluble in cold water or even in very warm water and which will make merchantable leather of superior quality, fine grain, and full and plump body, the last-named quality being the result of the second subjection of the skin to the alum and sodium-salt bath, thereby overcoming an insuperable objection heretofore existing—viz., the thinning of the skin by the action of the sodium hyposulfite after the first alum-treatment. If a superior quality of alum-

leather is desired, the skins taken from this final bath of aluminium sulfate and sodium salts are well adapted to be finished by the methods usually employed in finishing chrome-leather. If, however, it is desired to treat the tawed skin in the chromic compound, hereinafter described, to render it thoroughly insoluble in boiling water before subjecting it to any usual finishing method, my present invention comprises, as a final and fourth step in the process, the subjection of such alum-tawed skin to a bath of chrome-alum, in conjunction with sodium sulfate and potassium or sodium acetate, without the aid of any free acid, whereby the chrome-alum is decomposed when brought into the presence of the skin and the oxid of chromium is separated out in the presence of and insolubly combined with the previously-tawed hide-tissues, a result which has never before been accomplished with chrome-alum or previously-reduced chromic salts.

In the practice of my invention I use a drum as a preferable mechanical means of carrying out my process, as the tanning solution requires less water in such a device and is thereby more economically employed.

For every one hundred pounds of skins prepared for tanning I prepare a solution in two gallons of water of three pounds of aluminium sulfate and six pounds of fine common salt. This liquor is put in the drum with the skins and run for about half an hour. I then prepare a second solution by dissolving about ten pounds of hyposulfite of soda in about three gallons of warm water and add this solution to the liquor and skins still in the drum and run the drum for about fifteen or twenty minutes. I then prepare a third solution by dissolving about two pounds more of aluminium sulfate and three pounds more of fine common salt, and this solution is also added to the liquor and skins in the drum. The skins are now run in this liquor for a half hour or more, or longer, if need be, until the skins show by inspection that they have acquired the requisite plumpness. The skins are then taken from the drum and are preferably rinsed off by a single dipping of them separately in clean water and are then horsed up for several hours to drain.

The quantities of materials used as above

specified may be varied slightly in the three several steps, while retaining the proportions substantially as stated. For economy of operation I have described the three several solutions as being exhibited to the skins in the same drum in a certain order at intervals; but the same results are obtained if the skins are submitted to the three solutions separately but consecutively and in the order described.

The old liquor being drawn off from the drum, the skins (if not previously dipped in water when taken from the last alum-bath) are to be rinsed in clean water to remove any free acid or excess of tawing materials adhering to the skin from the previous bath. They are then again put back into the drum, into which my initially chemically neutral chrome liquor, hereinafter described, is to be introduced and without water or free acid of any kind. For this bath I employ not less than three nor more than six gallons of such chrome liquor to each one hundred pounds of skins. The chrome liquor is compounded as follows: I dissolve in five gallons of water from five to six pounds of chrome-alum, two and one-half to three pounds of sodium sulfate, two and one-half to three pounds of sodium chlorid, and twelve ounces to one pound of potassium or sodium acetate or its equivalent. The skins are run in the drum in this liquor for about an hour or until they have taken up all or nearly all the liquor and show thorough penetration of the chromic compound. At this stage they will be found to be perfectly insoluble in boiling water. They can then be removed from the drum and washed and finished, as usual in kid-leather dressing.

For heavy skins the neutral chrome liquor may be increased to six or even seven gallons to each one hundred pounds of skins. As the active sodium salt in this solution is the sulfate, the chloride being used only to prevent tightening of the skin fibers, the chlorid may be omitted if the sulfate of sodium is increased by an amount equal to one-half the weight of the chlorid as given in the above formula. It may also be observed that the quantities of each ingredient named may be varied slightly, provided the proportions stated be substantially retained.

Heretofore it has been proposed in the patents granted to Schultz, both dated January 8, 1884, to deposit the chromic oxid on the hide-tissues, insolubly combining the same therewith by presenting the chromic compound to the skin as chromic acid or as a bichromate in the presence of inorganic acid, and after impregnating the skin therewith to separate out the oxid by a chemical reduction of the acid by means of a sulfurous-acid-producing salt, such as hyposulfite of soda, in the presence of a decomposing acid; but this method requires as distinctive steps or features that the chromic salt when presented shall be an acidified or acid solution and not already reduced to an oxid, that there

shall necessarily be two separate, distinct, and sequential baths or presentations, that there shall be a free inorganic acid in one or both of the baths producing sulfurous acid from the sulfite and in the presence of the chromic acid to be acted upon and in quantity capable of chemically reducing the same and converting it into an oxid, and that this reaction shall take place on and in the presence of the hide to be treated.

The distinctive features of my process (which is radically different in every respect from the foregoing) are primarily that no free acids, either organic or inorganic, are employed, that the skin is first alum-tawed, and finally that it is treated with chromic oxid presented as an already-reduced salt, the oxid being separated out of the compound not by a chemical reduction, but separated out and insolubly combined with the previously-tawed hide-tissues by what is apparently a process of dialysis, this result being effected by combining with the chrome alum the requisite inorganic salts of sodium and the requisite alkali salt of an inorganic acid in suitable proportions, as stated.

The chemical reactions which take place are not well understood nor satisfactorily explainable in the light of present chemical knowledge, and this is due mainly to the fact that the presence of the organic matters of the skin to be acted on radically change the chemical equations.

It has long been known that chrome-alum and sodium sulfate perform a tawing function—*i. e.*, convert raw skin into leather; but the resultant product is open to various objections, principally the instability of the compound of chromium salts with the hide fiber, it being easily soluble even in cold water. When, however, a soluble organic acid compound is added to said elements in proper relative proportions and a skin is exhibited thereto, undoubtedly a new chemical reaction supervenes, (probably a separating out of chromic oxid and its precipitation in nascent condition in the hide fiber,) and the resultant compound is an insoluble one and capable of resisting the test with boiling water. That the skin itself acts in or is the initial cause of this reaction seems certain, as it will not take place in its absence. Why the organic acid compound produces the separating out and deposition of nascent chromic oxid when the skin is brought into the presence of a solution of the three elements I am unable to explain, even after a careful search in published technical works and inquiry of leading chemists; but I do know, however, that free acid in the solution, either organic or inorganic, added as an element—*i. e.*, other than as produced by the decomposition of the chemicals employed in the presence of the skins—will retard, if not prevent, the reaction described, and I have found after repeated trials that an alkali salt of an organic acid, such as acetate of potassium or sodium, is the most available to pro-

duce the desired result. While, however, I have specified sodium or potassium acetate as the particular salt of an organic acid which is to be used, I desire it to be understood that the corresponding salts of neighboring organic acids in the series, which are well understood to have in many respects similar properties, may be employed.

The hyposulfite of soda used in the described process is the salt commonly sold under that name, sometimes called by chemists "thio-sulfate of soda" and answering to the formula $\text{Na}_2\text{S}_2\text{O}_3$. The sulfate of alumina employed is that commonly sold under that name and sometimes as "concentrated alum," and it is usually united with sulfate of potash when sold as common alum; but in the latter case to carry out my process a double quantity thereof must be used. The chrome-alum employed is the commonly-sold lump chrome-alum of commerce and is usually a double sulfate of chromium and potassium.

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

1. In the art of alum-tawing, the process which consists in first subjecting skins prepared for tanning to the action of a solution of aluminium sulfate and of inorganic salts of sodium, then further treating such skins in an aqueous solution of hyposulfite of sodium, and finally adding to the bath a second solution of the ingredients first used but in a slightly-less quantity, the skins being successively acted upon by the bath in its several conditions substantially as described.

2. In the art of tawing, an initially-neutral composition for the production of insolubly-tawed skins which consists of an aqueous solution of chrome-alum, inorganic sodium salts, and a sodium or potassium salt of acetic or a neighboring organic acid of that series, substantially as specified.

3. A composition for the production of insoluble-alum-tawed skins by after treatment of such tawed skins with chromic salts, which consists of an initially-neutral aqueous solution of chrome-alum, sodium sulfate, sodium chlorid and potassium or sodium acetate, admixed in the proper proportion, substantially as specified.

4. In the art of tawing hides and skins prepared for tanning, the process described which consists first, in submitting them to the successive action of dissolved aluminium sulfate and an inorganic sodium salt, then to an aqueous solution of hyposulfite of sodium, then to the repeated action of aluminium sulfate and an inorganic sodium salt and finally drawing off the old liquor from the apparatus and subjecting the skins to the action of an aqueous solution of chrome-alum, inorganic sodium salts and a potassium or sodium salt of acetic or a neighboring organic acid of that series, substantially as described.

In testimony whereof I have hereunto affixed my signature this 29th day of March, A. D. 1897.

GEORGE W. ADLER.

Witnesses:

GEO. W. REED,
H. T. FENTON.