UNITED STATES PATENT OFFICE.

GEORGE W. ADLER, OF PHILADELPHIA, PENNSYLVANIA.

ART OF TAWING HIDES.

SPECIFICATION forming part of Letters Patent No. 573,631, dated December 22, 1896.

Application filed May 21, 1896. Serial No. 592,503. (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 the Art of Tawing Hides and Skins, of which the following is a full, clear, and exact specification.

My invention relates to the tawing of hides and skins in the manufacture of leather of all kinds and whether of light or heavy texture, and is applicable to the treatment of skins in all conditions, whether pickled, salted, dried, or fresh.

It has for its object the production of tawed skins and hides from which leather can be made by the usual subsequent treatment that will be practically insoluble in water, strong and durable, and readily adapted in the case of kid leather to take color and polish and presenting in the finished article a soft and velvety surface and with a fine close grain.

My invention consists in the improved compound and process hereinafter fully described and claimed, and is applicable to that stage in the art of making leather which comprises the tawing proper, that is to say, after the skins and hides are depilated by any of the usual methods commonly employed for the purpose and subsequently washed, pured, or branned.

If pickled skins are to be used in the manufacture, they may be milled in salt water, as usual, to remove the pickle, or they may be subjected in pickled condition to my tawing process and compound, depending somewhat upon the character and purpose of the leather which it is desired to produce therefrom; but so far as respects the application of my tawing process thereto it is immaterial whether the skins are milled in salt water or used in the pickled condition.

The principle involved in my process is the impregnation of the skin with a compound containing normal chlorid of chromium and sulfate of sodium with an organic acid, such as formic acid or acetic acid or their compounds, as the principal constituent active agents in the tawing process, the same being in such relation to each other that the chromium and sodium salts will each be severally capable of exerting its full tawing effect on the skin in the manner hereinafter mentioned, and each also of controlling or, rather, of qualifying the separate action of the other; and my invention further comprises, broadly, the method of forming such a compound of chlorid of chromium, sulfate of sodium, and an organic acid, as hereinafter described.

In carrying out my process a concentrated solution of the tawing liquor is prepared as follows: I first form a compound of sulfate of potassium or of sodium with chromic acid by dissolving a given quantity of bichromate of potash or of soda in one and a half times its quantity by weight of sulfuric acid, adding two parts by volume of water to one of acid, and this chromic-acid compound therein is then to be reduced to a sesqui-oxid (Cr_2O_3) by an organic reducing agent, such as sugar or alcohol, either of which I have found to be convenient for the purpose and particularly effective by reason of the presence of formic or of acetic acid, respectively, produced therefrom in the compound. To this resultant sesqui-oxid solution is then to be added a solution of carbonate of soda, whereby it is neutralized and sodium combined with it, the resultant being sodium sulfate and formate or acetate, chromic hydrate, and chromium oxycarbonate, the last two forming a precipitate, and this precipitate is then to be dissolved in the presence of hydrochloric acid, as hereinafter described, giving normal chlorid of chromium and sulfate of sodium with some sulfate of chromium, some chlorid of sodium, also some sulfate of potash, (if bichromate of potash has been employed in the initial composition,) and an organic acid, either formic or acetic, resulting from the decomposition of the particular organic reducing agent employed, combined with sodium as a formate or an acetate.

The following proportions and method of procedure will produce the results stated: Taking a given quantity of bichromate of potash or of soda, say five (5) pounds, it is to be dissolved in fully one and a half times that quantity by weight, say seven and one-half to eight pounds, of sulfuric acid, diluted with double the quantity by volume of water that there is of acid used, and this chromic-acid compound so admixed with sodium or potassium sulfate is then to be completely re-

duced to a chromic oxid the formation of which may be determined by the liquid assuming a decided dark-green color, for which purpose the quantities named will require about one pound of white sugar or one and one-half pints of alcohol, added slowly to keep the temperature below the point of ebullition and until effervescence ceases. The solution is then to be rendered neutral and sodium sulfate formed therein by adding to the quantity named about twenty (20) pounds of carbonate of soda dissolved in about seven and one-half ($7\frac{1}{2}$) gallons of water, the sodium-carbonate solution being added slowly until effervescence ceases and the mixture allowed to stand several hours until precipitation of the contained chromium oxycarbonate is completed. The final step in the preparation of the compound consists in adding hydrochloric acid to this solution containing the precipitate in quantity enough only to split up or decompose and completely dissolve all the precipitated chromium compound, the sodium compound being already in solution, and for this purpose about six to seven pounds by weight of such acid will be sufficient for the quantities named of the other ingredients employed, and twelve (12) to twenty-four (24) hours will be required for the purpose; but especial care must be taken that there shall be no excess of hydrochloric acid used beyond the quantity necessary to accomplish the object stated.

The solution thus compounded of the ingredients and in the quantities named will be of about 20° to 23° Baumé in density at about 60° Fahrenheit of temperature and will make ten (10) to twelve (12) gallons of the concentrated tawing liquor.

The solution is principally a normal chlorid of chromium with sulfate of sodium and an organic-acid compound such as formate or acetate, though I cannot define in chemical terms the exact character of the union of the several constituent elements. It will probably best be represented by the formula:

$$Cr_2Cl_6+Na_2So_4+K_2So_4+NaCl+NaCHO,$$

or

$$NaC_2H_3O_2,$$

or

$$Cr_2(CHO)_2,$$

or

$$Cr_2(C_2H_3O_2)_6,$$

and a quantitative analysis of the concentrated compound prepared as hereinbefore directed will show it to contain substantially the following: sodium sulfate about twenty per cent.; sodium chlorid and potassium chlorid together about seven per cent.; chromium chlorid about eight per cent., and of organic acids, in this particular instance as a formate of sodium, about two per cent. It is unnecessary to give all of the several reactions at each step in the formation of the compound, it being sufficient to state that the chromium as a sulfate, $Cr_2(So_4)_3$, neutralized by the carbonate of soda, ($3Na_2Co_3$,) will give a solution containing sodium sulfate and also a precipitate of chromium compound as above described. When this is acidified by the addition thereto of hydrochloric acid, the chromium precipitate contained therein is dissolved and changed into chromium chlorid as the constituent chromic salt. The organic-acid compound formed by the action of the reducing agent in the prior step is carried forward without change into the finally resultant composition.

The constituent double salts of chromium and sodium, it will be found in practice, are in this compound in such union and relation to each other and to the organic acid combined therewith, chemically considered, that they will each be severally capable of exerting their full effect as tawing agents (the sulfate salt of sodium being a far superior and differently-acting coadjutant of chromium salts for this purpose than the chlorid of sodium) and that each will modify the otherwise undesirable action of the other when used separately or in excess—*i. e.*, the sodium sulfate will qualify the usual astringent effect of the chromium salts and the chlorid of chromium will qualify or reduce the usual opening or swelling effect of sodium salt in excess—while at the same time the normal chromium salt in this compound will on contact with the organic substances of the hide give up the hydrochloric acid with which it is combined and be precipitated as an oxid, the reaction taking place in the fiber of the skin producing fixation and insolubility of the coagulated gelatinous tissues. Whether or not this peculiar action of the normal chromium chlorid (which proceeds without any deleterious effect on the skin and by what is apparently a process of dialysis) is due to the use of the normal chlorid of the metallic salt in conjuction with the particular sodium salt employed or solely to the presence of the organic acid in the compound, it is at least certain that such acid greatly aids and hastens the reaction stated and produces a rapidity of insoluble fixation that prevents any injury to the skin from the natural astringent action of chromium salts and results in the production of a remarkably fine and soft leather. It will also be found that the skin will rapidly and completely take up and absorb the tawing materials, the refuse liquor after the tawing is completed showing almost a complete deprivation of the contained salts.

The skins are to be submitted to a bath of this compound diluted to an extent varying according to the character of the skin to be acted on, the length of time of immersion also varying for the same reasons. Ordinarily this concentrated solution should be diluted to the extent of three to four times its volume of water in order to reduce it to a hydrometric strength of 5° to 6° Baumé. The tanner can easily determine when the skin is completely tawed by cutting into the thick-

est part of the skin and noting the penetration of the solution. The skins and hides treated by my solution so prepared will be found to be insoluble and perfectly tawed with a remarkably fine grain and surface.

The process as compared with a double-bath or two-step process will be found much cheaper, more certain in operation and result produced, and gives a better and more uniform quality of leather.

Any well-known modes of finishing the tawed skins for conversion into merchantable leather may be employed.

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

1. As an improvement in the art of tawing hides and skins, the subjection of the skin to the action of a bath containing chlorid of chromium, sulfate of sodium, and an organic-acid compound—such as a formate or an acetate; admixed substantially as set forth.

2. As an improvement in the art of tawing hides and skins, the submission thereof to a solution derived from an admixture of sodium sulfate and chromic acid, said acid being then reduced in the solution by an organic reducing agent, then neutralized by adding an alkali, and the precipitated chromic compound decomposed and dissolved in the presence of hydrochloric acid then added to the solution containing same, substantially as set forth.

3. The process of compounding a tawing liquor which consists in dissolving potassium or sodium bichromate in an excess of sulfuric acid diluted with two parts by volume of water to one of acid, reducing the solution by sugar or its alcoholic equivalent, then neutralizing and precipitating the same by the addition of carbonate of soda, and finally dissolving the contained precipitate by exhibiting hydrochloric acid thereto; substantially as set forth.

In testimony whereof I have hereunto affixed my signature this 19th day of May, A. D. 1896.

GEORGE W. ADLER.

Witnesses:
H. T. FENTON,
J. W. SHANNON.