

# UNITED STATES PATENT OFFICE.

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## PROCESS OF TAWING HIDES.

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*To all whom it may concern:*

Be it known that I, CHRISTIAN HEINZERLING, a subject of the Emperor of Germany, residing at 9 Rotteckstrasse, Frankfort-on-the-Main, in the Empire of Germany, have invented certain new and useful Improvements in Processes of Tawing or Tanning Hides, of which the following is a specification.

It has before been proposed to employ compounds of chromium or other mineral salts, but hitherto the employment of such substances has been accompanied by some disadvantages, namely: first, the leather is wanting in weight; second, the leather is thin and unfilled; third, the leather cuts rough instead of smooth; fourth, generally the leather is not sufficiently capable of resisting the influence of water.

In order to avoid the effect of washing the leather containing the tanning material (chromium or other mineral substance) was impregnated with fats or paraffin which made it less waterproof, or, when the tanning was carried out with chromic acid salts, they were reduced with green vitriol, oxalic acid, sulphurous acid, thio-sulphuric acid, sulphureted hydrogen, &c., a process which is only suitable for the manufacture of certain kinds of leather in which no value is placed upon a smooth cut and good weight. The reduction also of the chromic acid in acid solutions appears detrimental to the ultimate quality of the leather. Further, tanning with chromic acid salts or chromic oxide salts does not appear to have been sufficiently observed so that the different chromium compounds behaved very differently to the fibers of the hide. The tanning process hereinafter described is to obviate the above mentioned difficulties.

In place of the compounds of chromium heretofore employed I use substances containing a compound of chromic acid and chromium, that is to say chromate of chromium or chromate of chromium in which one or more atoms have been replaced by acid radicals. The following may be mentioned: chromic chromate  $\text{Cr}_2(\text{CrO}_4)_3$  formed either by dissolving chromic hydrate (one molecule) in the equivalent quantity of chromic acid (three molecules) or by decomposing a salt of chromic oxide with compounds of chromic

acid; bichromate monosulphate of chromium  $\text{Cr}_2(\text{CrO}_4)_2\text{SO}_4$  formed either by dissolving one molecule of chromic hydrate in two molecules of chromic acid and one molecule of sulphuric acid or by any other suitable methods; basic chromate sulphate of chromium  $\text{Cr}_2\text{CrO}_4\text{SO}_4$  formed by dissolving one molecule of chromic hydrate in a solution of one molecule of chromic acid and one molecule of sulphuric acid; chromate disulphate of chromium  $\text{Cr}_2\text{CrO}_4(\text{SO}_4)_2$  formed by dissolving one molecule of chromic oxide in two molecules of sulphuric acid and one molecule of chromic acid.

In combination with the above named compounds there may be used the alkaline salts of chromic acid already employed and chromic acid.

In carrying out the process of tanning, the hides to be tanned are prepared, cleaned and deprived of hair according to the usual methods. The hides thus prepared for tanning are first placed in a dilute solution of the above mentioned compounds of chromic acid and chromic oxide and then the solution is successively strengthened by putting in fresh quantities of the chromium compounds. It is preferable to begin with a one-fourth to one-half per cent. solution and gradually strengthen this to from ten to fifteen per cent. For heavy leather very concentrated solutions should be used at the finish.

The length of time of the tanning depends upon the thickness and quality of the hides. Heavy leather hides are left five to eight weeks in the tan liquor.

The above mentioned compounds may be used alone or the hides may subsequently be treated with one or other of the following compounds in order to give color and weight: aluminium chromate formed by dissolving an excess of aluminium hydrate in hot chromic acid; chromic thiosulphate by decomposing salts of chromic oxide with salts of thio-sulphuric acid; chromic sulphite either by decomposing salts of chromic oxide with neutral or acid sulphite salts or by saturating a solution of sulphurous acid with chromic hydrate; chromous chloride  $\text{CrCl}_2$  formed by reducing chromic chloride  $\text{Cr}_2\text{Cl}_6$  with zinc or iron; chromous sulphate  $\text{CrSO}_4$  formed by reducing chromic sulphate  $\text{Cr}_2(\text{SO}_4)_3$  with zinc

dust or iron filings; chromium thiocyanate formed by decomposing barium thiocyanate with chromic sulphate; ferrous thiosulphate  $\text{FeS}_2\text{O}_3$ , aluminium thiosulphate  $\text{Al}_2(\text{S}_2\text{O}_3)_3$ ,  
 5 zinc thiosulphate  $\text{ZnS}_2\text{O}_3$ , manganese thiosulphate  $\text{MnS}_2\text{O}_3$ , all four formed by decomposing barium thiosulphate  $\text{BaS}_2\text{O}_3$  with salts of sulphuric acid or in other suitable manners; Schützenberger's hydrosulphites also  
 10 called Bernthsen's hyposulphites:—ferrous hydrosulphite  $\text{FeS}_2\text{O}_4$ , zinc hydrosulphite  $\text{ZnS}_2\text{O}_4$ , manganese hydrosulphite  $\text{MnS}_2\text{O}_4$ , sodium hydrosulphite  $\text{Na}_2\text{S}_2\text{O}_4$ , formed by the action of the metal upon sulphurous acid or  
 15 bisulphite of sodium. When finishing with these compounds I begin with a weak solution of one-fourth to one-half per cent., and subsequently strengthen the solution to five to seven per cent. according to the thickness and kind  
 20 of leather.

In combination with the above named compounds there may be used the alkaline salts of chromic acid already employed or chromic acid itself.

25 Even the alkaline salts of hydrosulphurous acid effect the reduction of the chromic acid and its compounds without addition of acid which is not the case with the alkaline thiosulphates.

30 The metallic salts of hydrosulphurous acid especially those of iron and zinc are much more efficacious than the alkaline salts of the latter. The metallic salts thereby deposit metallic oxide which not only tans but also  
 35 gives color and they can be used as alkali salts without the addition of acid. The chromic and chromous oxide salts in use in my process reduce without any addition of acid the chromic acid and chromic acid compounds.  
 40 The chromous oxide salts mostly combine with the fibers of the hide. The leather produced is thereby fuller and cuts smoother, the tanning is more complete and the weight better than in the old method of chromate  
 45 tanning.

The above mentioned alkaline and metallic salts of hydrosulphurous acid are used in solutions containing from one-fourth to three per cent. of the salts according to the weight  
 50 and thickness of the hides.

Compounds of chromic chromate, chromate

sulphate of chromium, chromic thiosulphate, chromic sulphite are taken up so easily and in such great quantity by the fibers of the hide and are retained so well that they may  
 55 for some kinds of leather be used alone for tanning.

If it be wished to obtain a very complete tanning of the leather and good weight the above named combinations are preferably  
 60 used.

If it be wished to produce an especially hard and solid leather, hide tanned with the above mentioned chromium compounds is treated with barium thiocyanate, when by de-  
 65 composition there is formed chromium thiocyanate and the corresponding barium salt which for the most part is deposited on the fibers of the hide. The tanned hides for upper leather or other light leather should be  
 70 made therefrom, and as soon as they come out of the tan liquor should be well washed, greased and dressed according to the known methods.

If it be wished to produce colored or black  
 75 leather, the hides are dyed preferably before the greasing.

Hides intended for sole leather do not require washing but may be taken out of the tan liquor, dried and dressed in the usual way.  
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What I claim is—

1. The process of tanning hides consisting in subjecting them to the action of a solution containing a compound of chromic acid and chromium.  
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2. The process of tanning hides consisting in subjecting them successively to the action of solutions containing a compound of chromic acid and chromium and another compound of chromium, respectively.  
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3. The process of tanning hides consisting in subjecting them successively to the action of a solution containing a compound of chromic acid and chromium and then to a solution of a thiosulphate respectively.

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