UNITED STATES PATENT OFFICE.

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PROCESS FOR MANUFACTURING LEATHER.

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To all whom it may concern:

Be it known that I, FRIEDRICH WILHELM WEBER, a subject of the German Emperor, residing in the city of Perth Amboy, county of Middlesex, State of New Jersey, have invented certain new and useful Improvements in Processes for Manufacturing Leather, of which the following is a specification.

This invention relates to a process of tanning hides and relates particularly to the tanning processes applying a solution of a chromium salt as a tanning liquor. The object of the invention is to provide an improved and simplified process of tanning hides whereby a considerable saving both in money and time is obtained as well as a material of satisfactory qualities.

In the practice of my improved process the hides are first unhaired and are then "puered" which operation consists in paddling the same for instance in a weak warm infusion of fermented dog's dung or some substitute for the same; afterward the hides are pickled in the usual way, as for instance by treating them in a solution of salt and sulfuric acid, whereupon the hides are tanned with a basic chromium-salt in the presence of another salt as will be more particularly described below.

In the further course of my new process the hides are washed with a di-sodium phosphate solution containing sufficient sodium peroxid to form hydrogen peroxid as well as sodium hydrate, which latter neutralizes the di-sodium phosphate to sodiumtriphosphate and also simultaneously neutralizes the acid adhering to the hides; subsequently the latter are fat-liquored to be then finished in the usual way.

For the better understanding of my new process I shall describe by way of example one way of how I proceed to carry the same into effect.

12 calf hides are prepared by unhairing, puering, and pickling the same in the usual way and are then brought into a bath consisting of a solution of 4 kilos zinc sulfate in about 400 liters of water and of about 4 liters of the tanning liquor prepared as hereinafter described. Care is taken that the hides are well soaked with the solution and this may be effected by agitating the bath by any of the well known mechanical means as for instance by drumming in a tumbler the axis of which should be so constructed as to keep either steam, hot or cold water or even the tanning liquor proper, running into or through the same.

The tanning liquor proper consists of a rather concentrated solution of a basic chromium salt and is obtained by acting with 600 gr. H_2SO_4 on 2.4 kilo $Na_2Cr_2O_7 + 2H_2O$, pouring the reaction mixture into 1 liter of water and finally producing a chromium sulfate by adding 5,606 liters of a 37° Bé. solution of sodium bisulfite thereto until the mixture shows about 42° Bé.

The liquor thus obtained is of dark emerald green color; besides chromium sulfate it also carries sufficient sodium sulfate to keep the chromium sulfate in solution and the zinc sulfate in solution.

As already mentioned the hides should be kept floating during the entire time the tanning liquor is acting on the same, and as soon as it is found by the well known tests that they are well tanned, the hides are taken out of the bath and piled on a horse and permitted to remain there over night. After this the hides are rinsed in tepid water to hydrolyze the chromium compound which has entered the pores of the hides; subsequently the latter are passed into a neutralizing bath containing 400 grs. di-sodium phosphate (Na_2HPO_4) and 40 grs. Na_2O_2 dissolved in 400 liters of water. The sodium peroxid decomposes in the bath to sodium hydrate and hydrogen peroxid and owing to the former I obtain a perfect neutralization of the hides, especially as the oxygen separating from the H_2O_2 keeps the pores of the hides open to easily permit access of the neutralizing bath to the intercellular spaces of the hides; furthermore, the presence of the hydrogen peroxid also permits the convenience of oxidizing the last traces of any sulfite compound which may still be present. The hides are then passed from this neutralizing bath to a tank containing tepid water to rinse off the last residue of the neutralizing liquor. When this stage is reached the hides are absolutely neutral so as not to change the color of either a blue or red strip of litmus paper. In this state a considerable amount of the oxygen gas separated from the hydrogen peroxid is still re-

tained in the pores of the hide and this fact may be taken advantage of in my new process; the hides are passed once more through tepid water and while still wet are spread and treated with fat which is then acted upon by the oxygen gas in the pores, whereupon it is finished in the usual way.

The leather produced by my new process displays the desirable plump and soft feel and also answers fully the highest requirements of the market. This good result is chiefly due to the application of the tanning liquor described above, for the chromium sulfate of said liquor is in highly dissociated state and is therefore capable of being more thoroughly absorbed and having the chromium more strongly fixed by the hide, this fixing of the chromium being enhanced by the hydrolysis going on during the washing of the hides with tepid water subsequent to their having been treated with my tanning liquor.

A further factor contributing to the success of my new process is the presence of a zinc compound, as for instance zinc sulfate, in the tanning liquor, for the zinc sulfate exerts a beneficial influence due to its disinfecting properties as well as by increasing the solubility of the chromium sulfate in water, thus always offering a clear tanning liquor, which otherwise would contain the chromium sulfate just within the limits of its solubility in plain water.

Finally, the zinc sulfate, having penetrated the hide, is transformed into zinc phosphate during the floating in the neutralizing bath, whereby the pores of the hide are filled with a voluminous deposit as soft as silk; furthermore there is formed an inert salt of chromic oxid, chromium phosphate, within the intercellular spaces of the hide whereby the hide shows less tendency to shrink than if only a hydrate of chromic oxid had been deposited.

The presence of active oxygen in the form of hydrogen peroxid is also material in giving the leather produced by my process a superior smoothness inasmuch as it plays an important part in one of the final steps of finishing the leather, *i. e.*, during the treatment of the hides with the fat liquor. The oxygen included in the pores of the hide oxidizes the fats or oils with which the hides are covered in the same way as is done in the oil tannage in the "stoves" wherein the applied fat is oxidized by means of the oxygen in the air; the oxy-fatty acids, formed by the action of the oxygen, combine strongly with the tissue of the leather and enhance very considerably the quality of the product made by my new process. The oil tannage of raw wet hides has been known for a long time but it is rather surprising that a like effect may be obtained by oxidizing fats with oxygen, the fat or oil being put on hides having already undergone a regular tanning process.

Though I prefer to apply sodium bichromate in my new process and to reduce the same with sodium bisulfite in the presence of sulfuric acid, it is of course understood that I do not restrict myself exclusively to any of these materials but that I may just as well use potassium bichromate or any other soluble bichromate and that I may also apply the organic salts of chromium oxid in connection with my process and use as an acid for instance hydrochloric acid, hydrofluoric acid or other suitable acid. I have also found that I get the best results if I regulate the reduction of the chromium compounds in the preparation of the tanning liquor in such a way that a chromium sulfate is obtained having combined in the maximum two molecules of chromium oxid with three molecules of sulfuric acid, and in the minimum four molecules of chromium oxid to five molecules of sulfuric acid. The sodium bisulfite solution, which I employ in my process, may be substituted at any time by solutions of other sulfites or bisulfites, such as for instance of chromium sulfite, iron sulfite, etc., or by a corresponding quantity of sulfuric acid of whatever form and origin.

It is evident that it is immaterial in the operation of my process whether or not I add the ready made liquor to the tanning bath and accomplish the tanning process in one bath or whether I saturate the hides in the sodium bichromate solution and then submit them to the action of the reducing bath, whereby the tanning agent is formed in the interior of the skin.

Furthermore I may operate my new process according to the method usually called "working the liquors down the yard"—*i. e.*, the goods are removed from a relatively weak bath, of a set of usually three baths, to the next stronger one from which they are finally brought to the strongest; thus the goods move in one direction and the liquors in the opposite, the original strength of each of the baths being maintained by adding to the weaker bath corresponding quantities of the tanning liquor from the next stronger bath while the shortage in the strongest bath is made up by adding the required quantity of new tanning liquor.

The fine effect of the hydrogen peroxid obtained by the decomposition of sodium peroxid may of course also be obtained by the application of any other alkali or alkali-earth peroxid or also by any solution of hydrogen peroxid rendered alkaline by any agent which may be desirable in view of the neutralization of the leather. Finally I wish to state that I do not restrict myself to the use of zinc sulfate only, but I may

also apply any other soluble zinc salt which is capable of forming an insoluble phosphate.

I claim:—

1. The process of tanning hides, consisting in first preparing the hides in any suitable manner, then soaking them in a solution of a zinc salt and of a tanning liquor, said liquor consisting of a solution of a chromium salt, and subsequently neutralizing the hides in a solution containing a phosphate.

2. The process of tanning hides, consisting in first preparing the hides in any suitable manner, then soaking them in a solution of a zinc salt and of a tanning liquor, said liquor consisting of a solution of a chromium salt, and subsequently treating the hides with a solution containing a phosphate and hydrogen peroxid.

3. The process of tanning hides, consisting in first preparing the hides in any suitable manner, then soaking them in a solution of a zinc salt and of a tanning liquor, said liquor consisting of a solution of a chromium salt, and subsequently treating the hides with a solution containing a diphosphate and a peroxid sufficient to neutralize the diphosphate.

4. The process of tanning hides, consisting in preparing the hides in any suitable manner, then soaking them in a solution of a zinc salt and of a tanning liquor, said liquor consisting of a solution of a chromium salt, passing the hides into a solution of a diphosphate and a peroxid sufficient to neutralize the diphosphate, rinsing the hides thus treated and acting with fat on the oxygen retained in the pores of the hides while in the wet state.

5. The process of tanning hides, consisting in first preparing the hides in any suitable manner, then soaking them in a solution of a zinc salt and of a tanning liquor, said liquor consisting of a solution of a chromium salt having in the maximum 2 molecules of chromium oxid bound to three molecules of sulfuric acid and in the minimum four molecules of chromium oxid to 5 molecules of sulfuric acid, and subsequently neutralizing the hides in a solution containing a phosphate.

6. The process of tanning hides, consisting in first preparing the hides in any suitable manner, then soaking them in a solution of a zinc salt and of a tanning liquor, said liquor consisting of a solution of a chromium salt having in the maximum 2 molecules of chromium oxid bound to 3 molecules of sulfuric acid and in the minimum 4 molecules of chromium oxid to 5 molecules of sulfuric acid, and treating the hides with a solution containing a diphosphate and a peroxid sufficient to neutralize the diphosphate as well as any acid adhering to the hides.

7. In the process of tanning hides, the treatment of the hides with a tanning liquor containing a chromium salt carrying an acid corresponding as to quantity in the maximum 3 molecules and in the minimum 5 molecules of sulfuric acid bound to 2 and 4 molecules of chromium oxid respectively.

8. In the process of tanning hides, the treatment of the hides with a tanning liquor containing a chromium salt having in the maximum 2 molecules of chromium oxid bound to 2 molecules of sulfuric acid and in the minimum 4 molecules of chromium oxid to 5 molecules of sulfuric acid.

9. In the process of tanning hides, the method of preparing a tanning bath containing a chromium sulfate, consisting in preparing a mixture of a bichromate salt and sulfuric acid in water, treating the mixture with sodium bisulfite and combining the mixture thus treated with a solution of a suitable zinc salt.

10. The process of tanning hides, consisting in first preparing the hides in any suitable manner, then soaking them in a solution of a zinc salt and subsequently adding a solution of chromium sulfate to said solution.

11. The process of tanning hides, consisting in first preparing the hides in any suitable manner, then soaking them in a solution of zinc sulfate and subsequently adding a solution of chromium sulfate to said solution.

12. The process of tanning hides, consisting in first preparing the hides in any suitable manner, then soaking them in a solution of zinc sulfate, adding to said solution a solution of chromium sulfate and subsequently treating the hides with a solution containing a phosphate and hydrogen peroxid.

13. The process of tanning hides, consisting in first preparing the hides in any suitable manner, then soaking them in a solution of zinc sulfate, adding to said solution a solution of chromium sulfate and subsequently treating the hides with a solution containing a diphosphate and a peroxid sufficient to neutralize the diphosphate.

14. The process of tanning hides, consisting in preparing the hides in any suitable manner, then soaking them in a solution of zinc sulfate, adding to this solution a chromium sulfate, passing the hides into a solution of diphosphate and a peroxid sufficient to neutralize the said diphosphate, rinsing the hides thus treated and acting with fat on the oxygen retained in the pores of the hide while in the wet state.

15. The process of tanning hides, consisting in preparing the hides in any suitable manner, then soaking them in a solution of zinc sulfate, passing them into a bath consisting of a solution containing a bichro-

mate-solution and sulfuric acid, subsequently passing the hides into a solution of sodium-bisulfite, rinsing the hides and acting with fat on the oxygen retained in the pores of the hides while in the wet state.

16. In processes of tanning hides the step of treating the wet, freshly tanned hides with a hydrogen peroxid solution and subsequently acting with fat on the oxygen retained in the pores of the hides while in the wet state.

17. In processes of tanning hides, the step of increasing the solubility of chromium salt during the tanning process by combining its solution with that of a solution of a zinc salt in the presence of a suitable phosphate.

18. In processes of tanning hides the step of increasing the solubility of chromium salt for the tanning process by combining its solution with that of a solution of zinc sulfate.

19. In processes of tanning hides, the step of neutralizing the wet, freshly tanned hides by treating them with a solution of a neutral phosphate and a substance containing oxygen in available form.

20. In processes of tanning hides, the step of neutralizing the wet, freshly tanned hides by treating them with a solution of a neutral phosphate containing hydrogen peroxid.

21. In the process of tanning hides, the step of neutralizing the wet, freshly tanned hides by treating them with a solution of a diphosphate and a peroxid sufficient to neutralize said diphosphate.

22. In the processes of tanning hides the step of treating the hides with a solution containing a substance carrying active oxygen after said hides have been treated with the tanning liquor proper.

23. In the processes of tanning hides the step of treating the hides with a solution containing hydrogen peroxid after said hides have been treated with the tanning liquor proper.

24. In the process of tanning hides the step of treating the hides with a solution containing a substance carrying oxygen in available form and acting with fat on the oxygen retained in the pores of the hides while in the wet state.

25. In the processes of tanning hides the step of treating the hides with a solution containing hydrogen peroxid and acting with fat on the oxygen retained in the pores of the hides while in the wet state.

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

FRIEDRICH WILHELM WEBER.

Witnesses:
MARION E. SULLIVAN,
OTTO K. ZWINZENBERGER.