

# UNITED STATES PATENT OFFICE.

MARTIN DENNIS, OF BROOKLYN, NEW YORK.

## TANNING LEATHER.

SPECIFICATION forming part of Letters Patent No. 495,028, dated April 11, 1893.

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*To all whom it may concern:*

Be it known that I, MARTIN DENNIS, of Brooklyn, in the county of Kings and State of New York, have invented certain new and useful Improvements in the Art of Tanning Leather, of which the following is a specification.

My invention relates to the manufacture of leather.

10 It consists of a novel method of fixing the so-called gelatin of the hide or skin by means of a metallic oxide, and has for its object the cheapening and simplifying of the process of making mineral tanned leather, as well as the  
15 improvement of the manufactured product.

It has long been known that chromic oxide has the property of combining with hide gelatin to form insoluble and non-putrescent body, and is therefore capable of converting  
20 hides into leather. It has been but a few years, however, that commercial leather has been made by so-called chromic tannage, and there is still much room for improvement in this kind of leather as placed at present upon  
25 the market. In my process chromic oxide is presented to the hide gelatin in the state of a soluble combination in which it is so loosely held that it is readily given up to the gelatin, rendering the fixing of the latter both rapid  
30 and complete. The soluble combination which I use is designated by chemists as a basic or oxy salt. When to solutions of a number of the normal salts of chromium is added a quantity of a more powerful base, a part of the  
35 acid which was combined with the chromium base is taken away and the base is left in a combination which may be regarded as basic, that is, containing two or more equivalents of the metallic base or oxide, to one of the acid.  
40 In this case the excess of metallic base over what the acid would hold in the normal salt, is readily yielded to any body having an affinity for it. The effectiveness of my method, as far as the mere fixing of the gelatin is concerned, lies in bringing the latter in contact,  
45 in a neutral or nearly neutral solution, with a chromic oxide so held as to be readily taken up by the gelatin. This result is accomplished by solutions of the combinations which  
50 I have called basic salts of chromium, and they furnish the only practicable means of presenting to the hide gelatin, chromic oxide

in soluble form and yet not in stable combination with acids. When hides or skins properly prepared, are treated with a solution of  
55 one of these basic chromic salts the gelatin quickly takes up the excess of the chromium base, (in combination with which it is insoluble,) and leaves only the remaining normal salt in solution.

Attempts have been made to use chromic  
60 alum for converting hides into leather, but without practical success. When chromic alum is used, deoxidation or reduction is unnecessary, since the chromium exists in the  
65 alum in the oxide form, but as chromic alum is a very stable body, and gives up its chromic oxide with great difficulty, the process of fixing the hide gelatin by its means is exceedingly slow and unsatisfactory.

The central idea upon which the practicable  
70 methods of chromic tannage, other than mine, are based, is to impregnate the hide or skin with chromic acid, and then to reduce this acid to chromic oxide in the substance of the  
75 hide, by means of some reducing agent, for example, sulphurous or oxalic acids, sulphureted hydrogen or protosulphate of iron. The chromic acid is usually introduced into the  
80 hides or skins by immersing them in a bath, to which bichromate of potassium and a strong acid like hydrochloric, have been added. Chromic acid however is a powerful oxidizing  
85 and corrosive agent, and invariably does more or less injury to the hide or skin, and unless it is handled with very great skill and caution will produce leather which will become  
90 hard and crack and exhibit other defects. In fact the utmost care and experience often fail to prevent the finished leather from showing  
95 the destructive effect of this powerful chemical agent.

One of the probable causes of the deterioration of leather made by use of chromic acid  
100 is, that chromic acid itself appears to enter to a greater or less extent, into some sort of combination with the hide gelatin, in which combination it is not wholly reduced to chromic oxide by the sulphurous acid or other reducing agent employed, but after the leather  
is finished and placed upon the counter or manufactured into shoes, the oxidizing and destructive effects of the chromic acid become manifest, by its losing its strength and sup-



pleness and becoming hard and brittle and papery to the touch.

It is true that the above method as far as fixing the gelatin is concerned, although it is done in an acid solution, is very effective. In fact it is, outside of mine, the only practical way known of accomplishing that result. This effectiveness is due to the fact that chromic oxide (which is the real fixing agent) is formed by the reduction of the chromic acid while in actual contact with the hide gelatin. Therefore the gelatin can take up the chromic oxide while in the so-called "nascent" state, and thus accomplish in a solution, which is necessarily acid, what it could not easily do if the oxide were not formed in direct contact with it; for instance, as when the hide is treated with an acid or even neutral solution of a normal salt of chromium. But the destructive action of chromic acid on the fiber of the hide or skin (particularly when the highest skill is not employed) renders it extremely desirable to use a method in which the hide is not exposed to the action of chromic acid or other destructive chemical agent, or to intensely acid solutions of any kind, but in which the chromic oxide is brought in contact with the hide gelatin in a nearly neutral and mild solution, and yet in a form in which it can be easily and quickly taken up. All this is accomplished by my method, which I will now describe.

The salt of chromium which I have found well adapted for my purpose is the chloride, although other salts might be used, and this I use to illustrate my process in the following description: I first prepare a solution of common chloride of chromium. This may be done by dissolving the pigment known as chrome green and which is hydrated oxide of chromium, in commercial hydrochloric acid which has been diluted with an equal bulk of water, care being taken to use more chromic oxide than the acid will take up, in order that the resulting solution may be as nearly neutral as possible. About eight ounces of the commercial acid are sufficient to dissolve a pound of commercial hydrated oxide of chromium. To this solution of chloride of chromium I add slowly and carefully a solution of a more powerful base and for which purpose I prefer carbonate of sodium, or as it is known in the trade, "sal soda," until precipitation of chromic hydrate begins, or if carbonate of sodium is used, until rapid effervescence ceases. It usually takes about one-half pound of sal soda crystals to each pound of chromic oxide dissolved as above. I now have a nearly neutral solution of oxy or basic chloride of chromium. It may be considered as consisting of the normal chloride of chromium and chromic oxide in soluble combination, (free chromic oxide hydrated or otherwise being insoluble in water,) and a quantity of chloride of sodium formed by the union of a part of the acid which was in combination with the chromium, with the sodium base of the

carbonate of sodium, and which also serves a useful purpose, which will be mentioned later on. The hides or skins, after having been suitably prepared by soaking, liming, unhairing, baiting, washing, &c., are immersed in the solution of the oxy or basic chloride of chromium prepared as above, and of a strength of about three gallons of the concentrated solution to one hundred gallons of water. To the solution is also added, besides that formed by adding carbonate of sodium to the solution of chloride of chromium, a few pounds more of chloride of sodium (common salt) for the purpose of preventing the grain of the leather from drawing under the astringent effect of the chromic salt, and to facilitate the tanning action. The treatment of the hides or skins in the above solution is accomplished in a "paddle" or other equivalent apparatus, as it is quite necessary that they be frequently moved in order that the action of the chromic salt may be uniformly distributed. According to the thickness of the skins and the strength of the solution, this tanning process requires from about ten to forty-eight hours. Ordinary goat skins for the so-called dongola leather do well by running them in the paddle during the day, then allowing them to stand over night in the liquor, and run the paddle about an hour in the morning when the skins will be found well tanned. The strength of the chromic solution may be varied according to the thickness of the skins, and may be strengthened from time to time during the tanning operation if necessary. After the absorption of chromic oxide has ceased, and all the gelatin of the hide has been rendered insoluble by its combination with the chromic oxide, which condition is readily recognized by one familiar with leather making, the skins are washed in clean water, and are then agitated in a bath containing finely divided carbonate of calcium or its equivalent.

Instead of carbonate of calcium, carbonate of barium or the carbonates of lead, zinc, &c., may be used. When carbonate of calcium is used, the form known in commerce as whitening is well adapted. The object of agitating the skins with these carbonates which are insoluble in water, is, that every kind of acid present may be neutralized without subjecting the skins to the action of an alkaline bath. The skins may now be again washed, after which they are ready for the so-called fat-liquor, for drying previous to dyeing, or for any other of the processes belonging to the currier's art.

As my invention does not appertain to the beam house work, by which the hides or skins are prepared for tanning, and which would be substantially the same for my process as for any other method of tanning or tawing, I will not specify any particular procedure for that part of the tanner's work. Neither is it necessary to give directions as to the treatment of the skins after they are removed from the bath of suspended carbonate of calcium, for



it is as various as the different uses to which leather is put, and does not belong to the realm of tanning proper, with which alone my invention has to do.

5 Among the advantages possessed by my method may be mentioned the following:—

10 First. The tanning or fixing of the gelatin is effected entirely in one bath, instead, as in the old methods, of impregnating the skins with chromic acid in one bath, and then reducing the chromic acid to chromic oxide in another bath. Thus the labor of one handling is saved.

15 Second. The skins are not exposed to the destructive action of chromic acid, whereby the leather is stronger, has much more suppleness which it long preserves, shows a better grain and does not become tinny or pappy, as compared with the product of the ordinary method of chromic tannage.

20 Third. There are no offensive or suffocating smells evolved as when in the ordinary methods, the chromic acid is reduced to chromic oxide by the use of sulphurous acid or sulphureted hydrogen.

25 Fourth. Since my tanning bath is entirely non-corrosive there is no danger of allowing the skins to remain in it too long, and not nearly so much skill and care are necessary as in the old methods.

30 Fifth. Not only is there a saving in labor in my process, but my tanning bath is much cheaper than those of the old methods, since the chromic oxide in my tanning bath costs much less as prepared by me than as prepared from bichromate of potassium and a reducing agent in the old methods.

35 Sixth. The tanning is effected in my process in a bath, which is not strongly acid, as is always the case in the old methods in which chromic acid is employed. This nearly neutral bath is of great advantage to the skins and naturally assists the currier in the subsequent work of dyeing and finishing the leather.

45 In the foregoing specification and in the claims to follow, the term basic is meant to include metallic salts, which contain more than one equivalent of the metallic base to one equivalent of the acid, as above described, and in the claims, the terms carbonate of sodium and carbonate of calcium are meant to

include their chemical equivalents for the purpose specified.

The word "tanning" is meant to include 55 all methods of fixing or rendering insoluble the so-called gelatin of the hides or skins for the purpose of converting them into leather.

The gist of my invention consists broadly in the use, as a tanning agent, of a basic or 60 oxysalt of chromium. Specifically it includes the use as a tanning agent a basic or oxychloride of chromium. It also includes a tanning bath prepared by adding to a solution of chloride of chromium, carbonate of 65 sodium, or its equivalent, until the chromium salt is rendered basic. Further it includes the use of a bath for tanning containing both basic of chloride of chromium and chloride of sodium. And lastly it includes the process 70 of subjecting hides or skins in which the gelatin has been fixed by treatment with oxy or basic chloride of chromium to the action of a neutralizing bath of suspended carbonate of calcium.

I therefore claim—

1. In the manufacture of leather, a tanning bath containing a basic salt of chromium in solution, substantially as and for the purpose 80 set forth.

2. In the manufacture of leather a tanning bath containing basic chloride of chromium, substantially as and for the purpose set forth.

3. In the manufacture of leather, a tanning bath containing basic chloride of chromium 85 and chloride of sodium substantially as and for the purpose set forth.

4. In the manufacture of leather, the treatment of hides or skins as follows: first, fixing the gelatin in the properly prepared hide or 90 skins, by means of a bath of basic chloride of chromium; second, then subjecting the said hides or skins, to a bath of suspended carbonate of calcium, substantially as and for the purpose set forth.

In testimony whereof I have signed my name to this specification, in the presence of two subscribing witnesses, on this 28th day of September, A. D. 1892.

MARTIN DENNIS.

Witnesses:

HENRY S. KALISKE,  
CARLOS KALISKE.