No. 688,294. Patented Dec. 10, 1901.

H. CARMICHAEL.

PROCESS OF TANNING HIDES OR SKINS.

(Application filed Dec. 14, 1896.)

(No Model.)

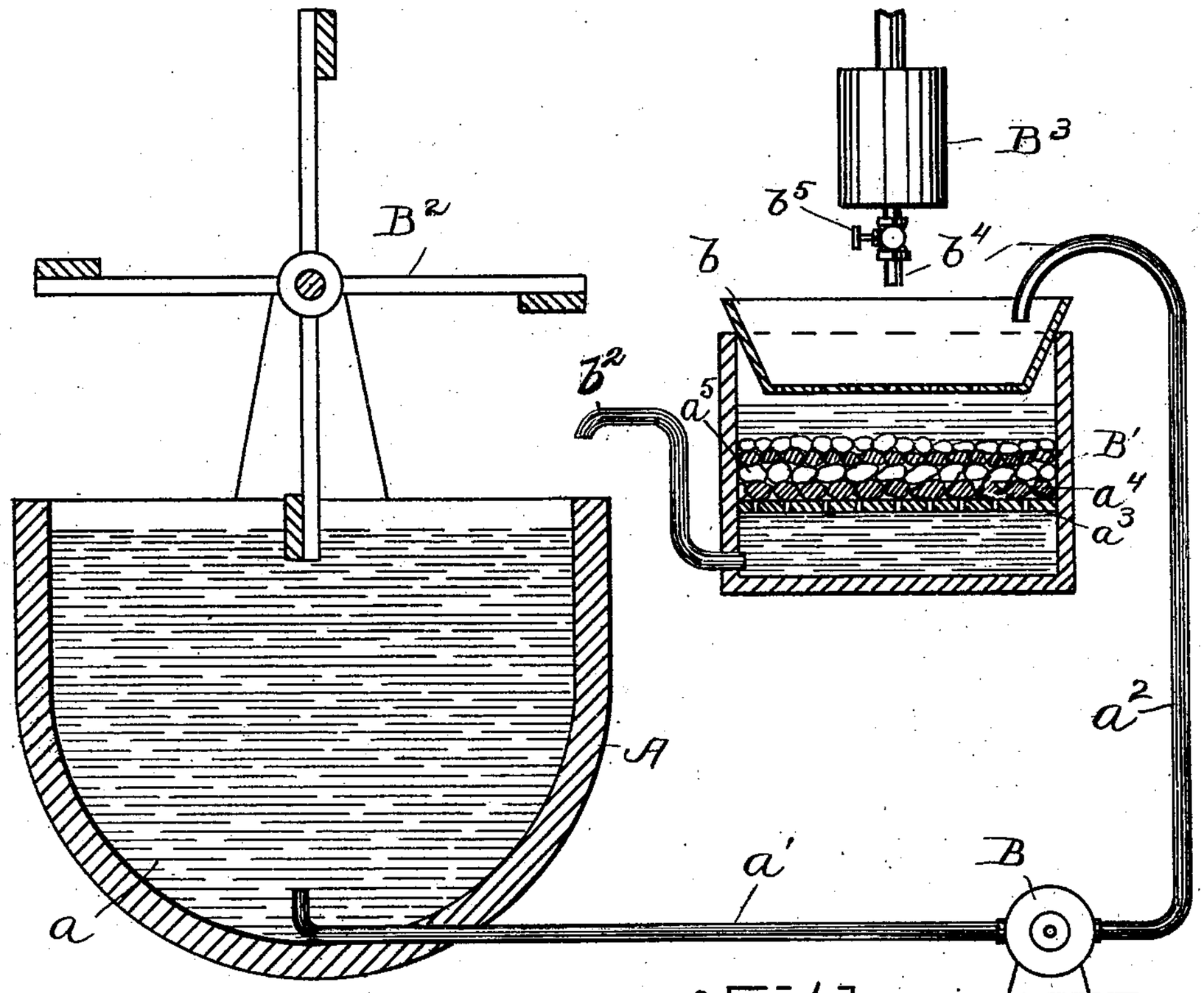

Fig. 1.

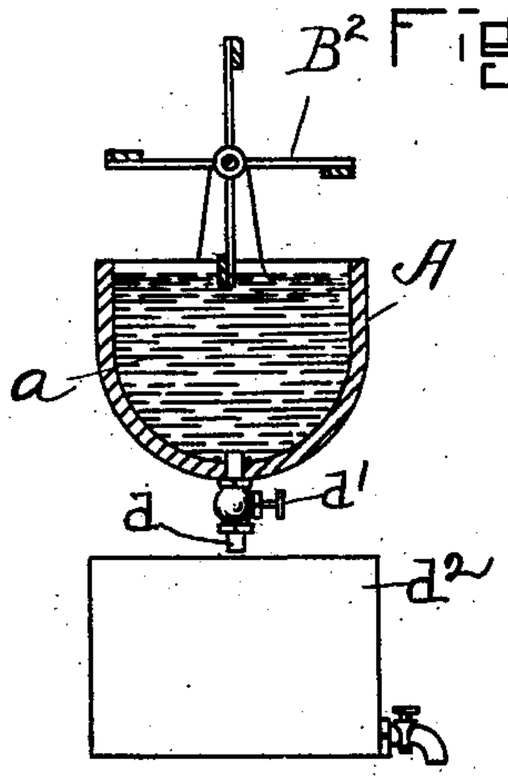

Fig. 2.

WITNESSES.

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HENRY CARMICHAEL, OF MALDEN, MASSACHUSETTS.

PROCESS OF TANNING HIDES OR SKINS.

SPECIFICATION forming part of Letters Patent No. 688,294, dated December 10, 1901.

Application filed December 14, 1896. Serial No. 615,549. (No specimens.)

To all whom it may concern:

Be it known that I, HENRY CARMICHAEL, residing in Malden, in the county of Middlesex and State of Massachusetts, have invented an Improvement in Processes of Tanning Hides or Skins, of which the following, in connection with the accompanying drawings, is a specification, like letters on the drawings representing like parts.

My present invention has for its object to provide a simple and efficient process for producing chrome-tanned leather, by which a product more uniform and of higher quality may be obtained without loss of skins or hides treated.

In accordance with this invention the hides or skins after being prepared in the usual manner for tanning are impregnated with a solution of chromic acid or chromic-acid compounds in a vat containing said solution, and after the hides or skins have become sufficiently impregnated, which may be determined in the manner now commonly practiced by cutting the skin in the thickest part, the skins are removed from the chromic-acid solution and placed in a second vat, where they are subjected to the action of a solution of a chromic salt, (sometimes termed "chromic-oxid salt,") preferably chromic chlorid, either neutral or basic, which gradually replaces the chromic acid or chromic compound in the hide or skin and being rendered insoluble in or upon the fiber produces a superior quality of leather. The chromic acid which is displaced slowly diffuses into the surrounding bath liquor. The solution of chromic salt, which may be hereinafter referred to as "chromic chlorid," is contaminated by the chromic acid diffused from the skin, and this contamination would present an obstacle for the carrying on of my process of chrome-tanning on a commercial scale owing to the excessively large quantity of chromic chlorid which would be necessary or required to effect the tanning if provision were not made to neutralize or offset the contamination of the chromic-chlorid solution by the diffused chromic acid, so that the tanning could be effected in a substantially small apparatus and with a substantially small quantity or volume of chromic chlorid. This result is effected in accordance with this invention by renewing or practically purifying the contaminated tanning solution, which renewal or purification is preferably accomplished in a separate chamber or vessel connected for convenience with the tanning-vat, so that the contaminated solution may be caused to pass through the purifying or converting chamber or vessel and then back again into the tanning-vat, the said contaminated solution on its passage through the purifying or converting chamber being freed from the contaminating chromic acid and restored to its original or normal chromic condition or state, which renewed chromic solution on its admission into the tanning-vat becomes again active in tanning the hide or skin. The chromic acid which contaminates the chromic solution may be disposed of by the action of any well-known reducing agent, but preferably by exposing it to the action of an oxidizable metal, such as zinc. To insure rapid action, the zinc is employed in a fine state of division and in the presence of more or less acid, such as hydrochloric acid, or it is made strongly electropositive by contact with gas-carbon or copper or by means of an outside source of electricity. The zinc is preferably located in the converting or purifying chamber or vessel. I prefer that the zinc or oxidizable metal in the purifying-chamber should be connected with pieces of electronegative metal. I prefer to use gas-carbon in contact with granulated zinc or with grids or bars of the latter metal to insure a prompt and energetic action on the contaminated chromic solution. The zinc in the converting or purifying chamber may be kept active or in an energetic condition by means of a free acid, preferably hydrochloric, which is supplied to the said chamber in such small quantities as will permit it to be practically exhausted by combining with the zinc before it passes, with the renewed chromic solution, from the purifying-chamber into the tanning-vat containing the hides or skins. The chlorid of zinc incidentally produced in the purifying vessel and which may be carried over into the tanning-vat does not appear to have any injurious effect upon the hide or skin.

Figure 1 represents in section and elevation a sufficient portion of one form of apparatus with which to practice this invention, and Fig. 2 a modification to be referred to.

Referring to the drawings, A represents a vat, which may be of wood or other suitable material and which in practice is designed to contain a solution *a* of chromic salt, preferably chromium chlorid, the said vessel, as herein shown, having connected to it near its bottom the inlet-pipe *a'* of a pump B, which may be of any desired or suitable construction and which is herein represented as a centrifugal pump. The pump B has its outlet-pipe a^2 extended over the upper end of a vat, chamber, or vessel B', provided with a perforated false bottom a^3, upon which is placed a layer of zinc a^4 and preferably a layer a^5 of gas-carbon or a bed composed of a mixture of these bodies. The vessel B' at its upper end is provided with a sieve or strainer *b* of any desired or suitable construction and upon which the liquid from the outlet-pipe a^2 for the pump is discharged. The vessel B' constitutes the converter or purifying-chamber of the apparatus herein shown and is provided with a liquid-outlet pipe b^2, connected to it below the false bottom a^3 and extended up preferably above the level of the layers of zinc and gas-carbon and terminates above the top of the vessel A, so that the liquid passing through the chamber B' may flow back into the tanning chamber or vat A. The vat A may and preferably will be provided with an agitator, herein shown as a paddle-wheel B^2, by which the hides or skins placed in the vat A may be kept in motion in the solution *a*. The converting or purifying chamber B' is adapted to be supplied with free acid, preferably hydrochloric, from a supply tank or vessel B^3, provided with a discharge-pipe b^4, having a cock or valve b^5, by which the supply of the free acid to the chamber B' may be controlled.

In the operation of the apparatus herein shown the hides or skins to be treated after being first impregnated with a solution of chromic acid or its compounds, as now commonly practiced, (and which solution may be composed of about five per cent. of bichromate of potash to the weight of the skins or hides and from two to three per cent. of thirty-five-per-cent. hydrochloric acid,) are removed from the chromic-acid bath or vat (not herein shown) and placed in the chromic-chlorid solution *a* contained in the vat A, when an examination of the thicker parts of the hides or skins in the chromic-acid bath shows that the said hides or skins are thoroughly saturated with the chromic-acid solution.

The chromic solution *a* may be made by dissolving commercial soluble chrome-green or hydrated oxid of chromium in a minimum amount of hydrochloric acid and making up the bath by an addition of water to a strength of about four-per-cent. solution of chromic chlorid, or the said bath may be made by passing a solution of bichromate of potash to which hydrochloric acid has been added through the vessel B' and diluting the bath to an extent to form about a four-per-cent. solution of chromic chlorid in the vat A. Common salt is preferably added to the solution in the vat A in about the proportion of two parts salt to one part of chromium chlorid to prevent the drawing of the grain and to facilitate diffusion.

The hides or skins saturated with the solution of chromic acid or its compounds are kept in motion in the tanning-vat A by the agitator B^2 or in other suitable manner, and while in the vat A the chromic acid contained in the skins diffuses into and contaminates the chromic-chlorid solution and imparts to the originally green chromic solution in the vat A a yellowish green tint, and the solution *a* contaminated by the diffused chromic acid from the skins is carried by the pump B to the converting or purifying chamber B' and discharged from the pipe a^2 upon the sieve *b*, which serves to prevent the passage of foreign bodies—such as loose animal fiber, hair, &c.—into contact with the layers of gas-carbon and zinc, through which the yellowish-green contaminated tanning solution percolates or passes and becomes freed from the contaminating chromic acid and converted into a purified chromic solution having nearly or quite an emerald-green color, which purified or renewed chromic-chlorid solution passes through the pipe b^2 back into the tanning-vat A, where it again becomes energetic and acts upon the fiber of the hide and is distributed with great uniformity through the thickness of the skin, replacing the chromic acid, which gradually diffuses out of the hide. This cycle of operations or steps is continued until the hide or skin has been properly tanned, and during the operation the color of the hide or skin passes from yellow to yellowish-green, then to sage-green, and finally to blue. When the thicker parts are colored blue throughout and pieces cut from them resist the action of boiling water without strong contraction, the tanning is completed. For many uses the resistant temperature of 80° centigrade suffices—that is to say, if the pieces cut from the hides or skins resist the action of water heated to 80° centigrade the said skins will be sufficiently tanned.

In the above process the chromic acid in the skin diffuses slowly out of the skin into the chromic-chlorid bath, the diffusion being resisted by the said bath, which latter seeks to penetrate into the skin to replace the chromic acid.

By the process above described the chromic compound is distributed with great uniformity throughout the thickness of the skins or hides, the grain is very perfectly preserved, and a strong and supple leather produced. The elasticity or extensibility of the leather can to a considerable extent be modified by the extent to which the process is carried and the product adapted to the various uses and methods of finishing leather. The time required to tan the hide or skin depends upon the thickness of the skin or hide, the strength

of the tanning solution, and the activity of the purifier or renewer. Goatskins can be tanned in twenty-two hours. The tanning bath or solution *a* may be used for a substantially long time, and many batches of skins or hides may be tanned in the same solution. It may be strengthened occasionally in case the chromic acid which diffuses from the skin is when converted in the purifier insufficient in amount to replace the chromic compound absorbed by the skin, and so, also, a portion of the contaminated solution in the vat A may be removed from time to time, so as to decrease the amount of zinc chlorid and other substances which may collect in the vat A. Furthermore, it is not necessary that the circulation be maintained through the purifier B′ throughout the period of tanning, for if after running the pump and paddle twelve hours or less the yellow color has disappeared from the skins and from the tanning solution the skins will continue to tan while the machinery is at rest.

I prefer to use the carbon as the electronegative metal; but I do not desire to limit my invention in this respect, as copper may be substituted for the carbon; but this is not deemed so desirable by me, as the chromic chlorid is found to exert a solvent action upon it and the skins are liable to be slightly discolored.

I prefer to use chromic chlorid; but I do not desire to limit my invention to this particular chromium salt, as other chromium salts, such as chrome-alum and chromic sulfate, may be used, but with lessened effects.

I prefer to effect the purification of the contaminated chromic solution in a chamber or vessel located outside of the tanning-vat; but, if desired, the chamber or vessel B′ may be suspended in the tanning liquid in the vat A and reliance placed on the difference of density of the liquids to establish circulation.

In order that my invention may be clearly comprehended, I have hereinafter set forth one set of proportions of the ingredients or materials used—namely, one hundred and fifty (150) pounds of bichromate of potash, one hundred and fifty (150) pounds of common salt, and six hundred (600) gallons of water are placed in the vat A. In the purifier B′ are placed two hundred (200) pounds of granulated zinc and six hundred (600) pounds of comminuted retort-carbon and in the vessel B^3 seven hundred and fifty (750) pounds of thirty-five per cent. (35%) of hydrochloric acid. The pump B is then started and circulation of the liquid in the vat A established through the purifier B′ and at the same time the valve b^5 is opened to supply the acid to the purifier in a slow stream. When the bath or solution in the vessel A has lost its reddish color and becomes emerald-green, the chlorid solution *a* is in proper condition for the reception of the skins, which to the weight of fourteen hundred (1,400) pounds can be floated in the above bath. During the process of tanning additional hydrochloric acid is supplied to the vessel B^3 and permitted to run slowly into the purifier.

In Fig. 1 I have showed a preferred form of apparatus in which the purifying or converting chamber is connected to the tanning-vat, so as to return the purified chromic-chlorid solution back into the tanning-vat, which is a simple, cheap, and efficient apparatus for carrying on this process; but the essential feature of this process does not depend upon the use of the purifying-chamber, inasmuch as the purifying-chamber, with the electropositive element, may be entirely disconnected from the tanning-vat A—as, for instance, in Fig. 2, the tanning-vat A is represented as provided with an outlet-pipe *d* at its bottom, having a cock or valve *d′*, by opening which the contaminated tanning solution may be allowed to run off into a second vat or vessel d^2, which may be designated a "waste" tank or vessel. The contaminated tanning solution discharged into the waste-tank may, for economy, be again purified by passing the same through a separate purifying-chamber; but this is not essential for the tanning of hides or skins in accordance with this invention, as a fresh supply of the chromic chlorid may be admitted into the vat A in proportion to the amount drawn off or discharged into the waste-tank.

I claim—

1. The method of tanning hides or skins, which consists in subjecting the hide or skin impregnated with chromic acid or its compounds, to the action of a solution of a chromic salt such as chromic chlorid, and continuing the action of the chromic chlorid upon the hide or skin by maintaining the chromic-salt solution practically free from the contaminating influence of chromic acid diffused from the skin, substantially as described.

2. The method of tanning hides or skins, which consists in immersing the hides or skins impregnated with chromic acid or its compounds, in a solution of a chromic salt in a vat or vessel, and continuing the action of the chromic salt upon the hide or skin by maintaining that portion of the chromic-salt solution, which acts on the hide or skin, substantially free from the contaminating effect of the chromic acid diffused from the skin, substantially as described.

3. The method of tanning hides or skins, which consists in immersing the hides or skins impregnated with chromic acid or its compounds in a solution of chromic salt in a vat or vessel, withdrawing from said vat or vessel a portion of the chromic solution contaminated by the chromic acid diffused from the skin or hide, purifying the withdrawn solution from the chromic acid, and returning the purified chromic solution to the said vat or vessel, substantially as and for the purpose specified.

4. The method of tanning hides or skins, which consists in subjecting them to the suc-

cessive actions of, first, an aqueous solution of chromic acid or chromic-acid compound, and second, to the action of a solution of a chromic compound, such as chromic chlorid, while the latter solution is being, part by part, exposed to the action of an oxidizable metal made electropositive in the presence of an acid, such as hydrochloric, substantially as described.

5. The method of tanning hides or skins, which consists in subjecting them to the successive actions of, first, an aqueous solution of chromic acid or chromic-acid compound, and second, to the action of a solution of a chromic compound, such as chromic chlorid, while the latter solution is being, part by part, exposed to the action of metallic zinc made electropositive in the presence of an acid, substantially as described.

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

HENRY CARMICHAEL.

Witnesses:

JAS. H. CHURCHILL,

J. MURPHY.