

UNITED STATES PATENT OFFICE.

HENRY SCHMID, OF MÜLHAUSEN, GERMANY, ASSIGNOR TO THE FIRM OF C. H. BOEHRINGER SOHN, OF NIEDER INGELHEIM, GERMANY.

PROCESS OF TANNING SKINS AND HIDES.

937,720.

Specification of Letters Patent.

Patented Oct. 19, 1909.

No Drawing.

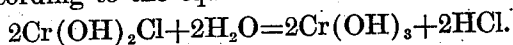
Application filed December 4, 1907. Serial No. 405,026.

To all whom it may concern:

Be it known that I, HENRY SCHMID, chemist, a citizen of the Swiss Republic, residing at Salvatorstrasse, Mülhausen, in Alsace, Germany, have invented certain new and useful Improvements in Processes of Tanning Skins and Hides, of which the following is a specification.

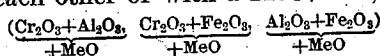
My present invention relates to improvements in the art of tanning skins and hides by means of metallic oxids, and it has for its object primarily to provide an improved process of this character whereby the leather obtained is unusually strong and is capable of being quickly dyed, the metallic oxids being so intimately introduced into the fiber of the skin as to render them perfectly fast.

The methods hitherto known of this kind of tanning and of tawing hides and skins had in view a combining of the animal skin with a metallic oxid or basic metallic oxid of the formula Me_2O_3 . In chrome tanning, for instance, the skins are impregnated with a basic chromic salt. In the same measure as chromic oxid or hydroxid is fixed on the fiber, acid is set at liberty, for instance according to the equation



This acid also adheres to the skin and penetrates it. In the known processes it is generally neutralized by means of borax or alkali silicate.

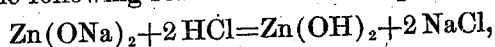
Now it has been found in the dyeing arts that the metallic sesquioxids of the formula Me_2O_3 such, for instance, as Cr_2O_3 , which act as mordants, act more effectively in combination with metallic oxids of the formula MeO , (for instance ZnO), although such oxids do not act as mordants. Such binary or ternary compounds which have been termed double and triple mordants wherein a sesquioxid may also be combined with two oxids MeO , or several sesquioxids with each other or with a MeO oxid, viz:—



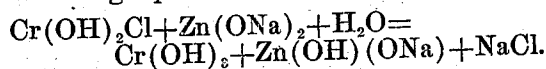
have affinities for pigments which are unknown or at least have not been utilized in connection with simple oxids. They also produce lakes of greater intensity and higher resisting power due, it seems, to the fact that the combined oxids adhere more strongly to the fiber and therefore combine with it more intimately. Such binary and

ternary compounds are, for instance, compounds of the formulæ $Cr_2O_3.MgO$, and $Al_2O_3.MgO.ZnO$. Experiments made with these combined mordants in mineral tanning demonstrate that a particularly strong leather is obtainable which permits an unusually fast dyeing, especially when fast mordant-dyes are employed.

According to the present invention the hides may be first tanned in the ordinary way, for example, with a basic salt of chromium oxid such as a basic sulfate or a basic chlorid of chromium, but instead of neutralizing the acid thus set free by means of borax or alkali silicate or the like, as has been said is usual in the known processes, the hide is now treated with the alkaline solution of another metallic oxid insoluble in water, for instance, with an aqueous solution of sodium zincate $Zn(ONa)_2$. Thus the following reaction would take place:

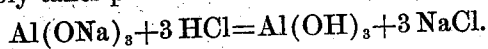


but the whole reaction, including the chromic salt, may be represented for instance by the following equation:



Thus the soda of the sodium zincate or a part of it combines with the portion of the acid radical not already neutralized, both chromic oxid and zinc oxid being set free and precipitated simultaneously in the skin. As a result, a more complete action of the chromic oxid is obtained and, moreover, this chromic oxid is more intimately combined with and enriched by the zinc oxid, the compound thus produced being more intimately fixed on the skin or hide than are the simple oxids. By the formation of this double dye-lake a more intense, lasting and deeper coloring is effected with a smaller quantity of dye.

Instead of using a sodium zincate solution, other solutions might be employed which have a similar chemical action. For instance, a solution of aluminate of soda or an ammoniacal solution of copper of chemically equivalent quantities might be employed, and in such case the following reaction probably takes place:

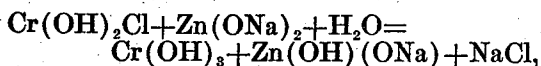


A similar action will take place when using

a solution of copper oxid in ammonia, but an exact chemical equation of the reaction which takes place in the latter instance cannot be given because such ammoniacal solutions of copper are not of uniform composition. By using the turkey red oils the fatty acids may also be precipitated, thus rendering the leather softer and more impervious. In this instance the fatty acids combine with the metallic hydroxids $\text{Al}(\text{OH})_3$ or $\text{Zn}(\text{OH})_2$ to form metallic salts, which also may be deposited on the fiber.

As an example of a process carried on in accordance with my present invention, the following may serve as an instance which will enable those skilled in the art to practice the invention. After the skins or hides have been prepared for tanning, that is to say, after they have been washed, depilated, and freed of lime, they are placed in a bath of basic chromic chlorid of 1° Baumé. About every fifteen minutes so much "chrome extract" is added that the concentration of the tanning-bath is increased by 0.25 or 0.5° Baumé each time, until it has reached about 3° Baumé. By "chrome extract" is meant mixtures consisting chiefly of basic chlorid of chromium or of basic sulfate of chromium or of a mixture of these chrome salts. Such mixture may also contain chlorid of sodium or sulfate of sodium, according to the method of preparing the extract. By cutting through a portion of the skin, the condition thereof may be determined, and when a sample cut indicates that the skins are completely tanned throughout the thickness, they are taken from the bath and transferred to a bath containing a sodium zincate solution of 2° Baumé. Every 20 minutes so much sodium zincate is added that the concentration of the bath is increased by 0.5° Baumé each time, until it has reached 4° Baumé, 80 minutes being thus required for the treatment. The skins or hides are then well washed and subsequently worked in the usual manner.

The combined use of salts of different metals such, for instance, as acetate of aluminium or chromium with those of lime or magnesia, has been practiced heretofore. Such prior processes differ from the present invention in the following respects: According to the present invention, basic metallic salt is exposed to the action of the metallic salt dissolved in caustic alkali. By the reaction,



a thorough and immediate deacidification of the basic salt takes place until an insoluble compound, or a metallic hydroxid, separates, and at the same time the oxid dissolved in alkali is set free and is deposited on the fiber of the skin in such an intimate rela-

tion therewith as to render it very adhesive. The metallic salts absorbed by the skin are thus deacidified and precipitated by means of a suitable alkaline double compound such, for instance, as sodium zincate $\text{Zn}(\text{ONa})_2$, sodium aluminate $\text{Al}(\text{ONa})_3$, and at the same time, the precipitated oxid, such as $\text{Cr}(\text{OH})_3$, is enriched by the oxids which are separated from the alkaline double compounds. The sodium aluminate is employed in exactly the same manner as has been described in the case of sodium zincate. As a result, the oxids are so intimately embodied in the skin as to render them perfectly fast, the results being superior to the previous method of neutralizing the basic salts by an alkali or by insoluble carbonates such, for instance, as prepared chalk.

Another advantage obtained by the present invention is, that a larger percentage of the various metallic oxids is introduced into the fiber of the skin, thereby increasing the percentage of tanning metallic oxid.

I claim as my invention:—

1. The herein described process of tanning skins and hides by means of metallic salts, which consists in impregnating the prepared skins and hides with the solution of a basic salt of a sesquioxid, and then treating the impregnated skins and hides with the alkaline solution of another metallic oxid insoluble in water.

2. The herein described improvement in the art of tanning skins and hides by means of metallic salts, which consists in impregnating the prepared skins and hides with the solution of a basic salt of a sesquioxid, and then treating the impregnated skins and hides with the alkaline solution of another metallic oxid of the formula MeO insoluble in water.

3. The herein described improvement in the art of tanning skins and hides by means of metallic salts, which consists in impregnating the prepared skins and hides with the solution of a basic salt of a sesquioxid, and then treating the impregnated skins and hides with an alkaline solution of sodium zincate.

4. The herein described improvement in the art of tanning skins and hides by means of metallic salts, which consists in impregnating the prepared skins and hides with the solution of a basic salt of a sesquioxid, and then treating the impregnated skins with the alkaline solution of another metallic oxid insoluble in water in which a soluble oil is dissolved.

In testimony whereof I have hereunto set my hand in presence of two subscribing witnesses.

HENRY SCHMID.

Witnesses:

W. A. LEONARD,
WILH. GÖHRIG.