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TANNING COMPOSITION MADE FROM A BASIC CHROME SULFATE AND A TRIS(HYDROXYACETATO)CHROMIATE

John Thomas Chain, Chardon, and John H. Pierce, Painesville, Ohio, assignors to Diamond Shamrock Corporation, a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

A composition for use in the tanning of leather comprises the reaction product of a basic, predominantly cationic, chromium-containing compound and a predominantly anionic chromiate. Typically this is the reaction product of a basic chromium sulfate and tris(hydroxyacetato)chromiate.

This invention relates to a new and improved composition for the tanning of leather and more particularly relates to a new and improved chromium-containing tanning composition and to the method of using it.

Generally, the major portion of leather tanning in the United States is accomplished using the so-called "chrome" tanning method. Before hides or skins are subjected to chrome tanning a number of preliminary treatments usually are performed on the hides or skins to ensure as complete a tan as possible. Basically, the hides which are removed from the animals are first cured which comprises partially dehydrating the animal hides with a salt, e.g., sodium chloride, or by drying them in air to arrest the action of bacteria thereon and thereby prevent their deterioration. The cured hides are next soaked in water or an aqueous solution to rehydrate the protein in the hides and remove the curing salt in the case of salted hides and clean off surface filth. After the hides have been soaked properly, they are immersed in a dehairing solution which generally has as its major constituent hydrated lime, $Ca(OH)_2$. The hides are allowed to remain in contact with the dehairing solution until the hair can be removed satisfactorily.

Following the dehairing process, the hides are subjected to bating, i.e., the action of proteolytic enzymes. Generally, synthetic bates are employed in conjunction with an inert material, e.g., wood flour, sawdust, etc., which serves as an enzyme adsorbent, and neutral deliming salts. When the hides leave the lime dehairing solution they have a pH of about 12.5. Bating, besides improving the properties of the hides, lowers their pH to approximately 8.0 to 9.0, the optimum pH for proteolytic enzymatic action. In order to bring the pH of the bated hides to a point where most chrome tanning operations are effective without the precipitation of insoluble chromium-containing salts from the tanning solution, i.e., a pH below about 4.0, the bated hides are pickled, i.e., soaked in an acid-salt solution, e.g., a solution of sulfuric acid and sodium chloride, until equilibrium between the pH of the solution and the pH of the hides is established. Generally, the equilibrium pH is within the range of about 1.5 to 3. Pickling removes most of the alkali fixed in the hides during the liming step. Also, pickling brings the hides into a uniform chemical and physical condition throughout its area and prevents a too rapid tanning of the hides.

After the hides have been pickled for a time sufficient to bring the pH of the hides below about 4.0, the hides are tanned generally in a solution containing chromium salts in one form or another, i.e., cationic, nonionic or

anionic. When the hides are near the end of the tanning cycle a small amount of a mild alkali, e.g., sodium or ammonium bicarbonate or borax, is added to aid in fixing the chromium in the hides. Following chrome tanning the leather may be treated further, e.g., washing, neutralization, dyeing, fatliquoring, etc., before being made into leather goods.

As can be readily seen from the above description many processing steps are necessary to prepare properly hides prior to the actual tanning with chromium-containing compounds. Thus, the elimination of one or more of these steps will enable the tanner to reduce the time necessary to produce leather and accordingly, reduce labor and equipment costs. It has now been found that leather characterized by a good color, fullness, and workability may be prepared utilizing a chrome tanning composition comprising the reaction product of basic, predominantly cationic, chrome salts, e.g., chromic sulfate, chromic chloride, and a chromiate compound, i.e., a chromium-containing compound where the chromium is believed to be predominantly in anionic form, e.g., di(oxalato)chromiate, tris(oxalato)chromiate, tris(hydroxyacetato)chromiate, and the like. The preferred tanning composition of the present invention comprises the reaction product of tris(hydroxyacetato)chromiate and chromic sulfate.

The tanning composition of the present invention exhibits a rapid penetration and fixation of the chromic oxide in the hides and a high alkali precipitation point. This later fact enables a tanner, by the use of the tanning composition of the present invention, to avoid the necessity of pickling hides prior to the chrome tanning step. As mentioned hereinabove, generally it is necessary to bring the pH level of the hides, prior to tanning, below a pH level at which chromium compounds form a permanent precipitate. It has been found that if the pH of the hides remains above this level, chromium salts precipitate from the tanning solution and effective tanning of hides is prevented. However, by employing the tanning composition of the present invention, the reduction of the pH level of the hides after bating is not an essential step to obtain an effective tan of the hides. It has been found that by using the tanning composition of the present invention, precipitation of chromium compounds does not occur if the hides are tanned directly after bating without the need of the intermediate pickling step. Accordingly, the tanning composition of the present invention enables a tanner to obtain an effective chrome tan in less time than was previously possible.

Basic chrome sulfate may be prepared by a variety of methods, but generally all involve the reduction of chromium from the hexavalent to the trivalent state. The two methods most commonly employed use either glucose or sulfur dioxide as the reducing agent of an aqueous bichromate solution. For example, to an aqueous solution of sodium bichromate is added acid followed by the required amount of glucose. This mixture is allowed to age to permit the various chrome compounds formed to become stable in the composition. The reduction of bichromate with sulfur dioxide consists of introducing sulfur dioxide into an aqueous bichromate solution and heating the reduced chrome liquor to remove any excess, residual sulfur dioxide. After the heating, the chrome liquor is allowed to age to ensure that the system has reached equilibrium.

The chromite compound may be prepared by reducing a chromium-containing salt, e.g., sodium bichromate, chromic sulfate, potassium chrome alum, with a carboxylic acid, e.g., oxalic, tartaric, hydroxyacetic, lactic, gluconic, etc. If desired, this reaction may be carried out in the presence of alkali, e.g., sodium hydroxide, barium hydroxide, etc. For example, one method of preparing

tris(hydroxyacetato)chromiate is by reacting barium hydroxyacetate with chromic sulfate or potassium chrome alum in aqueous solution followed by removal of barium sulfate, thus producing an aqueous solution of the desired salt. Another method comprises reacting hydroxyacetic acid with sodium bichromate in an aqueous solution producing the desired product. The reaction temperature is suitably controlled in the reactor to maintain the temperature below about 70° C., and preferably within the range from room temperature up to about 65° C. Since this reaction is exothermic, agitation means should be employed to dissipate the heat throughout the reaction mixture. Additionally, cooling means can also be employed.

The preferred tanning composition of the present invention comprises the product resulting from reacting basic cationic chromic sulfate with anionic tris(hydroxyacetato)chromiate. The proportions of the reactants which are employed depend on the amount of trivalent chromium, calculated as Cr_2O_3, contained in the sulfate and chromiate compounds, respectively. In general, the weight ratio of trivalent chromium, calculated as Cr_2O_3, supplied by the sulfate and chromiate compounds, respectively, should be within the range of about 10:1 to 1:1, preferably within the range of about 2.5 to about 7.5:1 with an especially preferred ratio of about 5:1.

The tanning composition of the present invention may be prepared either by mixing together the chromiate and sulfate or first mixing with a chromium salt, e.g., sodium bichromate, sufficient reducing agent, e.g., sugar or sulfur dioxide, to reduce approximately one-half of the chromium salt from the hexavalent to trivalent state and then subsequently mixing this mixture with hydroxyacetic acid. The reaction mixture is maintained in the reactor for a period of at least about 24 hours to insure substantially complete reaction before use.

In carrying out the tanning in accordance with this invention, the pH of the tanning solution may be maintained within the range of about 1 to 10 with a range of about 1.5 to 8 being preferred. Using the tanning composition of the present invention, it has been found that no neutralization of the tanning system is necessary if the stock, which is employed, is delimed to a pH within the range of about 8.5 to 9. The amount of tanning composition used is generally about 1% to 5%, preferably 2% to 3%, trivalent chromium, calculated as Cr_2O_3, of the tanning solution.

Tanning can be carried out at ordinary room temperatures, i.e. 70° F., up to about 90° F. to 100° F. Although it will be appreciated that in some applications higher tanning temperatures in the order of about 110° F. may be employed, the upper temperature limit generally is dictated by the quality of the leather which is required.

The time required for tanning in accordance with the practice of the present invention depends on a large number of variables, including the type of stock, thickness, prior treatments and effects desired so that a satisfactory "shrink temperature" can be obtained. Because of the faster penetration of the tanning composition of the present invention than basic chrome sulfate, the tanning time required is thereby shortened. As a general guide, however, it is desirable to subject the hides to the tanning solution of the present invention for a period of at least about 1 hour, typically for a period of time within the range of about 1 to 8 hours, and preferably up to about 5 hours at the temperatures indicated hereinabove.

It is to be understood that by the term "shrink temperature" is meant the elevated temperature at which shrinkage of the leather in water or a glycerine-water mixture first is observed. This temperature is used as a measure of tanning effectiveness. For instance, a "shrink temperature" of 200° F. or higher indicates a satisfactorily tanned leather.

Following the tanning with the tanning solution of the present invention, the thus-tanned hide may, if desired, be retanned with either a vegetable tanning material, a conventional chrome-tanning material, a combination of chrome and vegetable retans or the tanning composition of the present invention. If desired, the leather may be used without further treatment or it may be fatliquored, and/or waterproofed prior to usage with or without any of the aforementioned retannings.

In order that those skilled in the art may better understand the composition and method of the present invention and the manner in which it may be practiced the following specific examples are given.

EXAMPLE 1

(A) Preparation of tris(hydroxyacetato)chromiate

To 152.4 parts, by weight, of glycolic acid (Technical grade 70%)is added 120 parts by weight of a 50% aqueous solution of sodium bichromate. This reaction mixture is agitated continuously and the temperature of the reaction does not exceed 70° C. The final reaction product is blue in color and analyzes as follows: 13.14% by weight Cr_2O_3; 16.0% basicity (A.L.C.A.); 4% cationic Cr; 48% anionic Cr; 48% nonionic Cr; pH 3.2; specific gravity 1.4.

(B) Preparation of tanning composition

The tris(hydroxyacetato)chromiate prepared in Part A is divided into two equal portions. To one portion is added an equal amount, by volume, of Cr_2O_3 from "Tanolin KXD" and to the other portion an equal amount, by volume, of Cr_2O_3 from "Tanolin R." These two commercial tans are produced by the Diamond Alkali Company. "Tanolin KXD" and "Tanolin R" contain cationic chromium sulfate, by the reduction of sodium bichromate with sugar and have the following analyses:

Tanolin KXD

	Percent
Cr_2O_3	25.0
SO_3 (hydrolyzable)	21.1
Basicity	46–48
Na_2SO_4	28.6

Tanolin R

Cr_2O_3	23.5
SO_3 (hydrolyzable)	24.0
Al_2O_3	1.6
Basicity	34–37
Na_2SO_4	26.0

Basicity is defined as the percent of total chrominum present which is linked to hydroxyl groups. The two tans mixtures are blended thoroughly using continual agitation means. The blended tan reaction product is allowed to age for at least 24 hours before using.

EXAMPLE 2

Stock, consisting of pickled calf skin, is cut into matched pieces and floated in a tanning drum in a 3%, by volume, aqueous sodium chloride solution for a period of 10 minutes. To the 3% salt solution is added enough of the tanning agent to provide the tanning bath with 2% trivalent chromium, calculated as Cr_2O_3. Additional water is added to make 100% float. The pH of the tanning solution is about 2.5. Tanning is carried out on the calf skins for two hours at 100° F., after which time a 5% aqueous solution of sodium bicarbonate is added incrementally to the tanning drum over a period of an additional 2½ hours in an amount of 3%, by weight, of the stock raising the pH of the tanning solution. Tanning is continued for a total of 4½ hours after which time shrink temperatures are observed and recorded in Table I, below.

TABLE I

Run	Tanning liquor	Final pH	Shrink temperature, ° F.	Percent Cr_2O_3 fixation
1	Tris(hydroxyacetato) chromiate.	4.2	204	2.65
2	Tris(hydroxyacetato) chromiate-Tanolin KXD.	4.4	Boil	3.39
3	Tris(hydroxyacetato) chromiate-Tanolin R.	4.5	Boil	3.30

EXAMPLE 3

Example 2 is repeated except that during tanning the pH of the tanning bath is raised to 5.1. The results are presented in Table II, below.

TABLE II

Tanning liquor: Tris(hydroxyacetato)chromiate-Tanolin R	
Initial pH	3.0
Final pH	5.1
Shrink temperature, ° F.	Boil
Percent Cr_2O_3 fixation	3.24

EXAMPLE 4

This example illustrates that the tanning composition of the present invention gives a faster tan than either tris(hydroxyacetato)chromiate or Tanolin R. Example 2 is repeated except that after 2 hours of tanning, shrink temperatures are taken. The tanning composition and shrink temperatures are presented in Table III, below.

TABLE III

Tanning composition	Final pH	Shrink temperature, ° F., after 2 hrs.	Final shrink temperature, ° F.
Tris(hydroxyacetato) chromiate	4.25	208	210
Tris(hydroxyacetato) chromiate-Tanolin R	4.3	Boil	Boil
Tanolin R	4.0	180	207

EXAMPLE 5

This example illustrates that effective tanning is obtained using the tanning composition of the present invention without the need of the pickling step.

Two cowhide sides are bated for 1 hour at 95° F. in a bating solution containing 1% Oropon bate, a synthetic bate extracted from the pancrease of a hog, and containing trypsin as the active proteolytic enzyme. The delimed sides have a pH of 8.4 and weigh about 48 pounds each. To a 100% float is added 3% sodium chloride and a sufficient amount of the tris(hydroxyacetato)chromiate-Tanolin R reaction mixture (15.3% Cr_2O_3) to provide the tanning bath with 2% Cr_2O_3. After 3 hours the chrome is struck one-third of the way through the hides and after 6 hours, three-fourths the way through. The hides are allowed to stand overnight in the tanning solution. The next morning the sides are removed from the tanning solution. The tanning solution analyzes a pH of 4.0. The tanning results are reported in Table IV below.

TABLE IV

pH of Side	Flank sample [1]	Neck sample [2]
Grain	4.1	4.1
Flesh	4.1	4.6
Shrink temperature, ° F	Boil	208

[1] Flank struck through evenly.
[2] Neck not struck through evenly.

It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the full intended scope of this invention as defined in the appended claim.

What is claimed is:

1. A tanning composition comprising the reaction product obtained by chemically reacting basic chromium sulfate and tris(hydroxyacetato)chromiate in amounts such that the weight ratio of chromium, calculated as Cr_2O_3, supplied by said sulfate and said chromiate, respectively, to said reaction product is within the range of 2.5 to 7.5:1.

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DONALD LEVY, Primary Examiner

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