T. S. PERRIN

METHOD OF PREPARING A TANNING COMPOSITION COMPRISING
BASIC CHROMIC SULFATE
Filed Sept. 8, 1953

Na₂Cr₂O₇·2H₂O
70% LIQUOR

REACTOR

95% H₂SO₄

CRYS'TALS PLUS
MOTHER LIQUOR

CENTRIFUGE

MOTHER LIQUOR

CRUDE CrO₃
CRYSTALS

DISSOLVE

ADD IN ORDER:
1. H₂SO₄ TO pH < 1.0
2. REDUCING AGENT
   (STOICHIOMETRIC
   AMOUNT)
3. BASE TO pH 2.75-3.5

REDUCED CHROMIUM
SOLUTION

DRY

TANNING SALT

INVENTOR

TOM S. PERRIN

ATTORNEY
METHOD OF PREPARING A TANNING COMPOSITION COMPRISING BASIC CHROMIC SULFATE

Tom S. Perrin, Painesville, Ohio, assignor to Diamond Alkali Company, Cleveland, Ohio, a corporation of Delaware

Application September 8, 1953, Serial No. 378,994

3 Claims. (Cl. 8—94.27)

This invention relates to an improved chromium-containing tanning substance and to methods of preparing the same.

It has long been known that chromium in its trivalent state, probably in the form of the oxide, has a fixing or tanning action on the hide or skin, and upon the chromium so acting on such substances, the hide or skin is "tanned" and becomes leather. The art of applying chromium-containing materials to hides or skins to make leather is quite old, and started with the use of highly acidic compounds of chromium which were subsequently neutralized in the hide or skin by addition thereto of basic materials. It was early found, however, that damage was done to the skin by the highly acid compounds, such as chromic acid, and that the tannage could, moreover, be accomplished more efficiently and better tannage obtained with a single treatment employing a basic chromium salt or "one-bath tan." This was taught in Dennis Patent No. 495,028, which patented the basic process in the art which is still employed today.

Following the development of the so-called "one-bath chrome tan," it was soon found, upon the development of the dichromate industry, that dichromate could be used as a source material for the one-bath chrome tan and could be placed in proper trivalent basic condition by reduction with sundry reducing agents, of which sugar and sulfur dioxide are exemplary and are commercially practiced. In accordance, therefore, with prior art methods of making one-bath chrome tans, a dichromate solution is treated with a reducing agent, such as sugar, and upon the completion of the reduction, the solution contains approximately 25% of chromium as Cr₂O₃ and considerable inert salt of sodium with the acid used in the process of manufacture, usually sodium sulfate, which material has no value except as an inert in the tanning salt. The solution so prepared is suitably dried either by spray-drying or other conventional drying means and, as such, is ready for shipping to a tanner, who makes up a tanning solution from it as needed.

The large amount of sodium sulfate which must be shipped with the reduced chrome has heretofore been regarded as a necessary evil, in that there was no feasible way of producing one-bath chrome tans from sodium dichromate, the commonest source of chromium for the purpose, without the accompanying sodium sulfate. It is true, of course, that some salt of some kind, is preferably present with the tanning material when the same is in contact with a skin to be tanned. Such salt aids in preventing the skin absorbing an undesired amount of water during tanning. It has no tanning function per se.

The cheapest salt for the purpose is sodium chloride which may suitably be combined with the tanning solution when it is made up. The prior art was forced to the expedient of employing the already present sodium sulfate as the tanning compound could not be obtained without it.

A further disadvantage of the material prepared in accordance with prior art procedures is that vanadium, present in various amounts and sometimes as high as 1% in sodium dichromate liquors, of necessity carries through the process and forms a part of the tanning salt. While in many cases the small amount of vanadium is of no great concern to the tanners, especially where the tanning salt is to be used for tanning light-colored leathers, the presence of vanadium, usually in the form of sodium vanadate, is definitely to be minimized, as it tends to give a dark, streaky cast to the leather and renders the same unmarketable.

In accordance with the present invention, the disadvantages previously existing in one-bath chrome tan materials have been removed by modification in the procedures employed to obtain the tanning salt. Thus, rather than employing expensive purified sodium dichromate crystals or previously purified solutions of dichromate as the source of chrome in the tanning salt, it has now been found that the crude chromic acid crystals obtained by the reaction of saturated commercial dichromate solutions with the least expensive acid is, in the reduction of the hexavalent chromium and subsequent drying of the solution such as by spray drying, is materially higher in chrome content and, accordingly, lower in sodium sulfate content and, moreover, is substantially entirely free of vanadium impurity since the vanadium impurity goes out with the mother liquor from the crystallization of chromic acid. The provision of a chrome-tanning salt which is higher in chromium content and lower in sodium sulfate permits the tanner, upon working up his tanning solutions, to use less of the tanning compound for a given tanning job and still have the same amount of chrome concentration in his tanning solutions. The savings in shipment costs and the like, therefore, are quite substantial.

Another advantage of the present invention lies in the fact that the crude material obtained by the reaction of a concentrated commercial dichromate solution with sulfuric acid, may itself be forwarded to the tanner and reduced by the tanner in his own tannery for immediate use as a chrome-tanning material, thus eliminating the drying step. In such case, no waste material, such as sodium sulfate, need be shipped, and the freight charges are, accordingly, minimized, especially where the tanner is operating on a large scale and can afford to take substantial quantities of the crude chromic acid material.

The present invention may be more fully understood from the flow-sheet attached hereto and from the following descriptive statement respecting the flow-sheet:

Initially, it is noted that while the flow-sheet sets forth the subject matter hereof in the terms of employing commercial (70%) sodium dichromate solution as a starting material, the principles of the present invention are applicable to dichromates of other alkali metals, such as lithium, potassium, rubidium, and cesium, though none of these is normally employed for tanning purposes, with the possible exception of potassium, since the sodium salt is the least expensive, and the insolubility which, in the tanning salt, being in the form of sodium salts, are of no significance to the tanning process such as.

In the flow-sheet, it will be noted that a saturated solution of sodium dichromate (70%) is combined with sulfuric acid in a suitable reactor. The concentration of the sulfuric acid may vary between 75-80% H₂SO₄ and oleum (104.5% H₂SO₄), preferably about 95% H₂SO₄.

The addition of the concentrated acid to the saturated sodium dichromate solution is suitably controlled to maintain the temperature in the reactor within the range of 50° to 65° C. The amount of the acid employed may vary within the range of 3 to 4.5 moles of H₂SO₄ per mol of sodium dichromate dihydrate, but it is of particular advantage in preparing a tanning salt in accordance with the method of the present invention, to minimize...
the presence of sodium acid sulfate in the material obtained and to obtain as much chromic acid in the crystallized material as is possible. In order to do this, the ideal ratio is of the order of 3.5 moles of H2SO4 per mol of dichromate, and this is preferred.

The reaction mixture may be maintained in the reactor for a period of at least one-quarter hour to insure substantially complete reaction to chromic anhydride. Retention times longer than this are not harmful since the reduction of dichromate is not complete without some loss of the chromic acid with reduced chrome. As all the hexavalent chrome is to be reduced in the next step of the process, no harm is done by further holding the material in the reactor.

The reaction mass comprising a magma of chromic acid crystals and mother liquor may be passed to a suitable means for separation of the chromic acid crystals from the mother liquor, for example, a centrifuge. The temperature maintained in the separation means, such as a centrifuge, suitable varies between 50° and 65° C., it being noted that it is preferable in the case of preparation of the tanning salt of this invention, to maintain the temperature at least above 50° C. to avoid over-precipitation of sodium acid sulfate with the chromic acid.

Washing of the crystals in the centrifuge may be employed if desired, but no special advantage accrues therefrom as the subsequent steps of the process, i.e., acidification and reduction substantially preclude any advantage of washing at this point.

When the material to be processed in accordance with the remaining steps of the method of this invention, is derived as a side stream from a chromic acid manufacturing process in which the main stream comprises high purity chromic acid, then the material at this point may be a washed, or otherwise worked-up, crude chromic acid acid crystal mass. Such working-up may include washing of the crude crystals as aforesaid or actual addition of sodium bichromate dihydrate as crystals or as liquor say in the form of a 70% solution. No advantage accrues to this process by such treatment, but the economic burden of processing a separate stream solely for the raw material to be worked-up into a tanning compound in accordance herewith, may well outweigh the minor disadvantages and increase in cost of the tanning compound which arises from processing a separated crude chromic acid crystal mass. It is, however, the preference of this invention to separate crystals from the mother liquor without further work-up.

At this point in the process, the intermediate product comprises a combination of chromic acid, sodium acid sulfate, and water, the chromic acid normally ranging between about 80%-95%. Sulfuric acid, by maintaining an acid:dichromate ratio of 3.5:1 and the holding temperature of centrifuging in excess of 50° C., a material having as little as 3% of bisulfate is obtained. This material is a crystalline, readily-soluble substance, the crystal size depending upon the method of precipitation but being of the order of that of common granulated sugar. If the material is to be processed immediately into a tanning salt, then no drying step is necessary at this point to remove the residual water; in some instances, if the material is to be kept for a too great period of time without further processing, drying may be dispensed with. Where, however, it is intended to ship the material to a different geographic point for further processing into a tanning salt, it is preferable to remove the water therefrom prior to packaging, which removal may easily be accomplished by heating the substance to 100° C. for a relatively short period of time.

Whether the tanning salt is to be prepared immediately or in the future, the above-described product is, when it is desired to prepare the tanning salt, dissolved in water to produce a substantially saturated solution thereof. Other substances may be added to the solution, if desired, such as aluminum sulfate for its known function in tanning. Sulfuric acid is added to the system to adjust the pH to below 1.0 and the chrome reduced by any convenient reducing agent, of which sulfur dioxide or sunryd organic materials, such as sugar, are exemplary. Following the reduction of the hexavalent chromium to trivalent chromium, the pH of the solution may suitably be adjusted to produce the desired basicity of the tanning salt, suitably in the range of pH 2.75-3.5, and then the solution may be dried by any desired means, such as application of heat thereto, spray-drying, and the like.

In the dried salt, the final product may contain in the order of 30% or more chromium as Cr2O3, as compared with a maximum of about 25% of chromium as Cr2O3, which can be obtained by preparing a similar tanning salt from sodium dichromate liquor by prior art practice. The difference is more substantial than actually would seem apparent from the figures involved, since in the prior art tanning salt, the remainder of the material is inert sodium sulfate which, as noted above, has no tanning value per se, but which must nevertheless be shipped to the point of use as a part of the salt. In the present instance, the additional amount of chromium in the tanning salt admits of shipping the less sodium sulfate and, moreover, admits of use of less tanning salt on actual point of use to obtain the same chromium concentration in a tanning bath. When a tanner is prepared to use the material, it is simply dissolved in water to the desired concentration and employed in a well-known manner for tanning skins.

In order that those skilled in the art may more fully understand the method of the present invention, the following specific examples are offered:

**Example I**

(A) 1270 gms. of sodium dichromate dihydrate liquor (70%) is treated with 1080 gms. of 95% H2SO4 with agitation and cooling to maintain the temperature at 65° C. The precipitation time is taken as 25 minutes, after which the crystals formed in the system are centrifuged. A yield of wet crystals is obtained in (A) above. 11.67 gms. of H2SO4 (95%) are added thereto. The reduction is carried on with 7.84 gms. of corn sugar syrup, the temperature being maintained by external cooling within the range of 70°-80° C. and agitation being continuous during the reduction. The pH at this point after reduction is found to be complete and is below 1.0, whereupon 6.5 gms. of sodium carbonate solution are added to bring the pH to 3.3. The material is placed in an evaporating dish and dried in an oven at 100° C. of moisture, the weight of material obtained having 32.89% of chromium, calculated as Cr2O3, and 0.018% of vanadium, calculated as V2O5, and but 4.97% of Na2SO4.

**Example II**

A comparable run is made from the same sample of liquor as the starting material of Example I. This run is in accordance with the best techniques known for reducing dichromate prior to this invention. Thus, 25 gms. of H2SO4 (95%) are combined with 35.8 gms. of Na2Cr2O7·2H2O liquor and reduced with 8.9 gms. of corn sugar syrup. The pH is adjusted to 3.2 and the solution spray-dried as before. A tanning salt containing 24.66% of chromium, as Cr2O3, and 0.064% of vanadium, as V2O5, and 25.47% of Na2SO4 is produced. While reduction by both organic and inorganic reducing agents has been described, it is also feasible in some instances to employ both types of reducing agents in the same reduction batch. This is especially true when for reasons of supply, or other reasons, it is desired to employ some SO2 in the initial phase of the reduction but not to complete the reduction with SO2 especially in view of the unreasonable large and unwanted amount of sulfate thereby produced in the final composition. In this case, only a desired amount of SO2 need be used such as
as that which is equivalent to production of basic chromic sulfate in the system, whereupon an organic reducing agent (such as sugar or any organic substance having reducing properties, viz., propanol), may be employed to complete the reduction.

This is a continuation-in-part of application Ser. No. 319,361, filed November 7, 1952, now abandoned.

While there have been described various embodiments of the invention, the methods described are not intended to be understood as limiting the scope of the invention as it is realized that changes therewithin are possible and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. The method of preparing a tanning composition comprising basic chromium sulfate, which includes the steps of providing a substantially saturated solution of an alkali metal dichromate, adding to said solution sulfuric acid in an amount of from 3 to 4.5 moles of H₂SO₄ per mol of alkali metal dichromate, said acid having a concentration substantially within the range of 78%–104.5% H₂SO₄ by weight, maintaining the temperature of the mixture of said acid and said solution substantially within the range of 50–65°C until CrO₃ crystals precipitate, separating said CrO₃ crystals from the mother liquor so as to leave a comparatively small amount of the mother liquor adhering to said crystals, dissolving said crystals and mother liquor in water to form a solution containing chromic acid, adjusting the pH of the chromic acid solution with a strong mineral acid to a value below 1.0, reducing the hexavalent chromium of said solution to trivalent chromium by applying an aqueous solution of a chemical reducing agent, adjusting the pH of said trivalent chromium solution with an aqueous alkaline solution to a point substantially within the range of 2.75–3.5, drying the aforesaid solution and recovering therefrom the resulting composition containing basic chromium sulfate.

2. The method of claim 1 wherein said dichromate is sodium dichromate and the chromic acid solution is adjusted to a pH value below 1.0 with sulfuric acid.

3. The method of claim 1 wherein the hexavalent chromium solution is reduced to trivalent chromium with an organic reducing sugar and the resulting solution is adjusted to a pH within the range of 2.75–3.5 with a sodium carbonate solution and the reduced chromium compounds are recovered by evaporating the water solution thereof.

References Cited in the file of this patent

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Inventor</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>556,325</td>
<td>Saddler</td>
<td>Mar. 10, 1896</td>
</tr>
<tr>
<td>688,294</td>
<td>Carmichael</td>
<td>Dec. 10, 1901</td>
</tr>
<tr>
<td>1,872,588</td>
<td>Hines</td>
<td>Aug. 16, 1932</td>
</tr>
<tr>
<td>2,034,256</td>
<td>Vetter</td>
<td>Mar. 17, 1936</td>
</tr>
<tr>
<td>2,110,961</td>
<td>Merritt</td>
<td>Mar. 15, 1938</td>
</tr>
<tr>
<td>2,178,874</td>
<td>Hervey</td>
<td>Nov. 7, 1939</td>
</tr>
<tr>
<td>2,335,365</td>
<td>Smith</td>
<td>Nov. 30, 1943</td>
</tr>
</tbody>
</table>

FOREIGN PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Country</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>586,874</td>
<td>Great Britain</td>
<td>Apr. 3, 1947</td>
</tr>
</tbody>
</table>