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# LEATHER TANNING AGENT AND PROCESS

John Harris Haslam, Landenberg, Pa., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This invention relates to a novel combination of matter, tris(hydroxyacetato) chromiate, and to its use as a leather tanning agent.

Although chromium tanning is a process which has been use for many years, the chemistry involved is not thoroughly understood. It is usually considered that only basic chromic salts such as $CrOHSO_4$ are tanning agents. Nonbasic salts such as chromic sulfate

$$(Cr_2(SO_4)_3)$$

do not tan leather. Aqueous chromium chemistry is quite complicated with various hydrates being formed along with hydrolysis and olation.

Chrome tanning agents are currently produced by reduction of chromates with (1) sugar or (2) sulfur dioxide. Those tanning agents produced by sugar reductions give leather of different qualities than do the sulfur dioxide reduced tanning agents. This has heretofore been considered to be due to mixed organic compounds which were complexed with chromium. This has given rise to considerable investigation of "masking agents," i.e., organic materials added to the chrome tanning agents to complex with the chromium and alter the tanning effect. Accordingly, much work has been done on the effects of formic acid, acetic acid, oxalic acid, etc., when added to chrome tanning agents. While various masking agents have been added to basic chromium salts, no work has been done with tris(hydroxyacetato) chromiate or related materials as tanning agents.

An object of this invention is to provide a new tanning agent which produces a high degree of tanning rapidly.

Another object is to provide a tanning agent which does not require close pH control, and still another object is to provide a tanning agent which is effective at high pH's and which allows process simplifications.

According to this invention tris(hydroxyacetato) chromiate, is used as a tanning agent. When tris(hydroxyacetato) chromiate tanning agent is used, close control of pH is not necessary, and the tannage may even be effective at pH's as high as 10. The tanning process is therefore simplified.

Tris(hydroxyacetato) chromiate can be produced in a number of ways. For example, it can be made by the reaction of 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. It can also be produced by the reaction of sodium hydroxyacetate with a chromic salt. In these cases the tris(hydroxyacetato) chromiate produced has the chromium in the anion and therefore is properly called a chromiate. The complex is quite stable to hydrolysis being unaffected at pH's as high as 11. At these high pH's the tris(hydroxyacetato) chromiate may exist as a salt, e.g., where the cation is a metal such as sodium.

The invention is illustrated further by means of the following examples. It will be seen from these examples that by the addition of hydroxyacetic acid salts to non-basic chromic salts, the latter which will not tan leather are converted to effective tanning agents. This should be differentiated from the addition of masking agents which is done to basic chromic salts. It has been



found, as shown in Example 3, that the addition of hydroxyacetic acid salts to a commercial tanning agent which is essentially $CrOHSO_4$, is not as effective as tris-(hydroxyacetato) chromiate. Therefore, the addition of hydroxyacetic acid salts to nonbasic chromic salts produces a quite different effect than does the addition of hydroxyacetic acid salts to basic chromic salts.

*Example I*

250 ml. of 0.336 M chromic sulfate solution were placed in a flask. In a beaker 39.9 g. of barium hydroxide ($Ba(OH)_2 \cdot 8H_2O$) and 27.5 g. of 70% hydroxyacetic acid were mixed. Considerable heat was evolved and while the mixture was still warm, it was added to the chromic sulfate solution with thorough mixing. The precipitated barium sulfate was removed by filtration. The pH of this solution was approximately 1.7. Evaporation of a portion of this solution gave tris(hydroxyacetato) chromiate, as a blue-black solid residue. 5 cc. portions were removed and pH raised with 1 N sodium hydroxide. Small pieces of pickled kidskin were placed in these solutions and agitated for 30 minutes. Additional sodium hydroxide was added as required to maintain the pH at the desired point. After 30 minutes the kidskin was removed, pressed between blotting paper to remove excess liquid and the shrink temperature determined. The shrink temperature (i.e. the minimum temperature at which marked shrinking of the leather is observed when the sample is heated in water) is a measure of the degree of tanning, the higher the shrink temperature the higher the degree of tanning. The following table shows the relationship between shrink temperature and pH of tanning in the experiments just described.

| pH: | Shrink temperature, ° C. |
|---|---|
| 1.7 | 78.0. |
| 4 | Above 100.0. |
| 6 | Above 100.0. |
| 8 | 86.0. |
| 10 | 62.0. |

*Example II*

255 g. of potassium chrome alum

$$(K_2SO_4.Cr_2(SO_4)_3.24H_2O)$$

was dissolved in 1200 ml. of water. To this was added 315 g. of barium hydroxide ($Ba(OH)_2.8H_2O$) and 218 g. of 70% hydroxyacetic acid previously mixed. Precipitated barium sulfate was removed by filtration. 5 ml. aliquots were removed and small pieces of pickled kidskin were tanned for 30 minutes at various pH's. pH was maintained by the addition of 1 N sodium hydroxide solution. The degree of tanning was determined by shrink temperature. The results were as follows:

| pH: | Shrink temperature, ° C. |
|---|---|
| 4.3 | 91 |
| 6.0 | 92 |
| 7 | 86 |
| 8 | 70 |

*Example III*

127.5 g. of potassium chrome alum

$$(K_2SO_4.(Cr_2(SO_3)_3.24H_2O)$$

was dissolved in 600 ml. of water. To this was added 109 g. of 70% hydroxyacetic acid and 40 g. of sodium hydroxide. Raw kidskin was agitated with portions of

this solution as described in Example 1. The shrink temperatures were as follows:

| pH: | Shrink temperature, ° C. |
|---|---|
| 4.3 | 98 |
| 6.0 | 83 |
| 7 | 77 |
| 8 | 67 |

For comparison with the foregoing, a commercial chrome tannage which was 50% $Cr_2(SO_4)_2(OH)_2$, the remainder being largely $Na_2SO_4$, was tested as a tanning agent in combination with sodium hydroxyacetate. 16.5 g. of this commercial tanning agent was dissolved in 100 ml. of water. 30 minute tanning of pickled kidskin with this solution at a pH of 3.6 produced a leather with shrink temperature of 88° C. To a 25 ml. portion was added 7.5 ml. of 5 N hydroxyacetate solution to give a hydroxyacetic acid/chromium mole ratio of 3:1. 30 minute tanning of pickled kidskin at a pH of 4.4 with this solution gave a shrink temperature of 81° C. It is apparent from these results that the addition of hydroxyacetate ion to basic chromic sulfate does not improve its effectiveness as a tanning agent and in fact may lessen it.

*Example IV*

Using the same reagents described in Example 3, the effect of hydroxyacetic acid to chromium ratio was determined. 127.5 g. of potassium chrome alum was dissolved in 600 ml. of water to produce a 0.425 M chromium solution. A 5 M solution of sodium hydroxyacetate was made up and various amounts added to aliquots of the chromium solution to produce the desired hydroxyacetic acid-chromium mole ratio. Kidskin was tanned as described in Example 3 and the shrink temperature determined. The results were as follows:

| HAA/Cr Mole Ratio | Shrink Temperature, ° C. | | |
|---|---|---|---|
| | pH 3.524 | pH 6 | pH 8 |
| 1:1 | 52 | 87 | precipitated. |
| 2:1 | 65 | 87 | Do. |
| 3:1 | 78 | 86 | 73. |
| 4:1 | 81 | 86 | 65. |
| 6:1 | 78 | 78 | |

It is apparent from these that approximately 3:1 hydroxyacetate:chromium mole ratio is necessary to prevent precipitation at high pH but that at pH of 6, 1:1 mole ratio produces an effective tannage.

*Example V*

Ten grams of chromic acid ($CrO_3$) was dissolved in 50 ml. of water and the resulting solution of chromic acid was slowly added to 38 g. of 70% hydroxyacetic acid. The reaction mixture became quite hot and a considerable evolution of gas occurred.

Five ml. of the resulting solution was removed and the pH was raised to 6 by adding 1 N sodium hydroxide solution. A small piece of pickled kidskin was agitated with this solution for 30 minutes. The kidskin was removed and pressed between blotter paper to remove excess solution. The shrink temperature was found to be 88° C.

*Example VI*

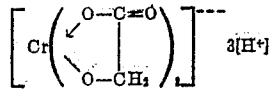
A solution of 14.9 g. of sodium dichromate

($Na_2Cr_2O_7.2H_2O$)

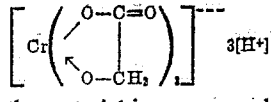
in 50 ml. of water was added slowly to 38 g. of 70% hydroxyacetic acid. The reaction was quite vigorous with considerable gas evolution. Three portions were removed and the pH was raised to 4, 6 and 8 respectively with 1 N sodium hydroxide solution. Small pieces of pickled kidskin were agitated in these solutions for the lengths of time shown in the following table and the shrink temperature determined. Additional sodium hydroxide was added during tanning to maintain the pH at the stated level.

| pH | Time (min.) | Shrink Temperature, ° C. |
|---|---|---|
| 4 | 30 | 100 |
| 6 | 30 | 86 |
| 6 | 60 | 89 |
| 6 | 1,200 | 100 |
| 8 | 30 | 72 |
| 8 | 60 | 77 |
| 8 | 360 | 86 |
| 8 | 1,200 | 89 |

The chemical structure of the tris(hydroxyacetato) chromiate in its completely ionized state can be formulated as follows:



or



Quite probably the material in aqueous solution is partially ionized, i.e. the species of ion above formulated is present in equilibrium with dihydrogen tris(hydroxyacetato)chromiate monovalent ion and monohydrogen tris(hydroxyacetato)chromiate divalent ion.

I claim:

1. Tris(hydroxyacetato) chromiate.

2. Process for chrome tanning leather which comprises employing tris(hydroxyacetato) chromiate as tanning agent.

**References Cited in the file of this patent**

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