United States Patent [19]

Erdmann et al.

[11] **3,714,211**

[45] **Jan. 30, 1973**

[54] **COMPLEX TRINUCLEAR METAL SALTS**

[75] Inventors: **Hans Erdmann**, Heidelberg; **Franz Friedrich Miller**, Ludwigshafen, both of Germany

[73] Assignee: **Badische Anilin - & Soda - Fabrik Aktiengesellschaft**, Ludwigshafen/Rhine and Rhineland-Pfalz, Germany

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[21] Appl. No.: **69,461**

[52] **U.S. Cl.** .....**260/438.5 R**, 8/94.26, 260/448 R

[51] **Int. Cl.**.....**C07f 11/00**

[58] **Field of Search** .....260/438.5 R, 448 R

[56] **References Cited**

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Primary Examiner—H. Sneed

Attorney—Johnston, Root, O'Keefe, Keil, Thompson & Shurtleff

[57] **ABSTRACT**

Complex trinuclear metal salts, methods for the production of these salts by reaction of salts of aluminum or of aluminum and trivalent chromium, which contain monovalent anions, with acrylic acid and the amount of an alkaline reacting agent necessary for their neutralization or with salts or acrylic acid and a method of tanning using these metal salts.

12 Claims, No Drawings

COMPLEX TRINUCLEAR METAL SALTS

The present invention relates to new salts which contain aluminum or aluminum and trivalent chromium as central atoms in a trinuclear complex cation, and acrylic acid anions as acido groups with or without hydroxo groups. The invention also relates to a tanning method using these complex trinuclear metal salts.

Similar complex trinuclear metal salts but with low saturated fatty acids (formic acid, acetic acid or propionic acid) have been proposed for aluminum as the central atom in Belgian Pat. No. 737,935 and for aluminum and trivalent chromium as central atoms in Belgian Pat. No. 736,165.

It is an object of the invention to provide tanning salts which cause a high shrinkage temperature and consequently improve the handle and flexibility of the leather obtained. Leather which is able to withstand the boiling test is obtained with these tanning salts. A particularly good property is that unsaturated carboxylic acids contained in the complex can be polymerized in the leather for example by means of redox systems. As a result there is the advantage that the leather has increased fulness and waterproofness in use and there is also the possibility in the subsequent ironing of the leather of carrying out the finishing without an additional operation.

The new salts are characterized by a cation having the general formula:

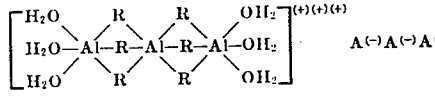
$$[M_a^1 M_{(3-a)2\,a)} R_m (OH)_{(6-m)}(H_2O)_3]^{(+x+x+)}$$

where M^1 denotes aluminum and M^2 denotes trivalent chromium, R denotes the radical of acrylic acid combined twice between two metal atoms, *a* denotes an integer from 1 to 3 and *m* denotes an integer from 2 to 6.

When *a* denotes the integer 3, pure complex trinuclear aluminum salts are obtained; when *a* denotes 2 or 1, mixed salts of aluminum and chromium are obtained.

The new aluminum or aluminum/chromic complex salts may contain any monovalent anions provided they do not make the complex insoluble in water, for example chloride, bromide, iodide, perchlorate, nitrate, formate, acetate and propionate ions. The complex salts according to the invention preferably contain chloride ions.

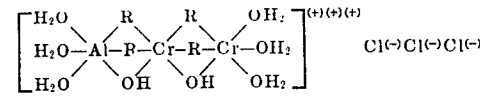
The aluminum complex salts have a structure in which, between the three central atoms, a total of six acido and hydroxyl groups, and at the two external metal atoms, three aquo groups in each case are coordinatively combined:



R denotes the acido radical of acrylic acid and A denotes a monovalent anion from the group given above.

The formula represents the μ-hexacido-hexaquotrialuminum salt $(Al_3R_6(H_2O)_6)A_3$. Up to four of the acido groups in the formula may be replaced by hydroxyl groups.

Aluminum/chromic complex salts in which one or two aluminum atoms are replaced by trivalent chromium atoms have the same structure, as for example μ-tetracido-μ-dihydroxo-hexaquo-monoaluminum-dichromic chloride:



The following are given as further trialuminum, dialuminum-monochromic or monoaluminum-dichromic complex salts having the same structure:

$[Al_3R_5(OH)(H_2O)_6]A_3$
$[Al_3R_5(OH)_3(H_2O)_6]A_3$
$[Al_2CrR_6(H_2O)_6]A_3$
$]Al_2CrR_4(OH)_2(H_2O)_6]A_3$
$]Al_2CrR_3(OH)_4(H_2O)_6]A_3$
$[AlCr_2R_5(OH)(H_2O)_6]A_3$
$[AlCr_2R_3(OH)_3(H_2O)_6]A_3$

$[Al_3R_4(OH)(H_2O)_6]A_3$
$[Al_3R_2(OH)_4(H_2O)_6]A_3$
$[Al_2CrR_5(OH)(H_2O)_6]A_3$
$[Al_2CrR_3(OH)_3(H_2O)_6]A_3$
$[AlCr_2R_4(H_2O)_6]A_3$
$[AlCr_2R_4(OH)_2(H_2O)_6]A_3$
$[AlCr_2R_2(OH)_4(H_2O)_6]A_3$

Complex salts according to the invention may be prepared in various ways. For example aluminum salts of monobasic acids alone or together with appropriate chromic salts in the molar ratio of chromium to aluminum given by the formula may be dissolved in water, and monomeric acrylic acid with an equivalent amount of an alkaline reacting agent, or the alkali metal salt of this acid, added in such an amount that at least 0.67 carboxylic acid radical and not more than 1.33 hydroxyl groups are available for each metal atom. The sum of the number of acrylic acid radicals and that of the hydroxyl groups should amount to 2.0 per metal. After the reaction is over, the complex salts formed may be processed into powder in a spray-dryer.

The sequence in which the said starting materials are brought together is not important. Thus it is immaterial for the production of salts according to the invention whether a start is made from solutions of the metal salts in acrylic acid while maintaining the above molar proportions or whether acrylic acid in the form of its alkali metal salts with or without alkaline reacting agents is added to metal salts of other monobasic acids or whether solutions of basic metal salts are treated with free acrylic acid. The setting up of the abovementioned molar ratios in the molecule is the decisive factor.

Increasing the proportion of acrylic esters in the form of the alkali metal salts per metal atom beyond the value 2 does not affect the formation of trimetal salts, but in this case water-insoluble products are obtained with the pure trialuminum salts devoid of chromium. The excess may cause an exchange of mineral acid anions of the trimetal salt for carboxylic acid anions or take no further part in the reaction with the present complex salts.

Adding alkali to a trimetal salt already occupied by acido groups causes a removal of the acido groups. An increase of the proportion of hydroxyl groups beyond the amount of 1.33 hydroxyl groups per mole of metal, however, results in precipitation. Conversely all the hydroxyl groups in a trimetal salt previously proportionately basified by adding alkali can be replaced by acido groups by the addition of free acrylic acid.

The alkaline reacting agents may be not only oxides and hydroxides of alkali metals and alkaline earth metals but also their carbonates. Examples are sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, calcium hydroxide, calcium carbonate, magnesium carbonate and dolomite.

The aluminum complex salts described herein are colorless. Mixed complexes of aluminum and trivalent chromium are pale green in powdered form, but greenish blue to ink blue in solution.

Salts according to the invention having the above formulas are outstandingly suitable for tanning. They have the advantage over prior art aluminum salts used for tanning that they are more resistant to hydrolysis. Therefore the material tanned therewith has a higher shrinkage temperature of 78° to 80° C, a great fullness and high suppleness of handle. Complex salts prepared with trivalent chromium give pale, light blue leather which withstands the boiling test.

These advantages are particularly valuable when salts according to the invention are used for tanning pelts which have been pretreated with aldehydes or agents yielding aldehydes. Aldehydes include especially formaldehyde, acetaldehyde, propionaldehyde, glyoxal and glutaraldehyde. Substances which split off aldehydes under the conditions of tanning may be used instead of the aldehydes or together with the same. These include sodium hydroxylmethanesulfonate, hexamethylenetetramine, paraformaldehyde, paraldehyde, metaldehyde and particularly N-methylol compounds, for example thos of urea, cyclic urea derivatives, melamine and dicyanodiamide. It has proved suitable to use the aldehydes in amounts of from 0.5 to 3%, preferably 1 to 1.5%, with reference to the weight of the material being tanned. Agents releasing aldehydes are advantageously used in amounts equivalent to the said amount of aldehyde or to the equivalent amount of aldehyde split off based in the equilibrium condition in solution.

Thus for example the pretreatment of pelts with 3% formaldehyde not only improves the handle properties of the finished leather and prevents the aluminum in the tan being washed out but also increases the shrinkage temperature to 88° to 90° C.

It is possible to prevent the acrylic acid radicals from being washed out by treating the leather obtained with a prior art redox system, for example persulfate/sulfite, and thereby polymerizing the acrylic or methacrylic acid radicals. Fullness and waterproofness of the leather are enhanced by this measure.

It has proved to be very convenient to use the salts according to this invention in amounts which are equivalent to 2.5 to 4% of Al_2O_3 (or Al_2O_3 and Cr_2O_3) based on the weight of pelts being tanned. In other respects, the same tanning conditions may be used with the salts according to the invention as are used with other aluminum tans. It has proved to be particularly advantageous to buffer the tanning liquor with alkaline reacting agents to a pH value of about 5 towards the end of the tanning.

The following Examples illustrate the invention. The parts and percentages specified in the Examples are by weight. Percentages by weight in the tan recipe relate to the weight of the pelts being tanned unless otherwise stated.

EXAMPLE 1

μ-triacrylatotri-μ-hydroxo-hexaquo-trialuminum chloride having the formula:

$$[Al_3(H_2C{=}CH{-}COO)_3(OH)_3(H_2O)_6]Cl_3.$$

72 parts of monomeric acrylic acid is added to a solution of 226 parts of a 66% basic aluminum chloride (22% of Al_2O_3) in 100 parts of water and the aged solution is spray-dried into a powder.

The product obtained in this way is a colorless powder having very good solubility in water. It contains an amount of sodium chloride originating from the reaction of aluminum chloride, in addition to the salt according to the invention.

The complex salt thus obtained is used for tanning cowhides according to the following specification:

Completely delimed and bated pelts are treated in 100% of aqueous liquor containing 10% of sodium chloride and 3% of 30% aqueous formaldehyde solution. Thirty minutes later 15% of triacrylato-trihydroxo-trialuminum chloride is added as a powder and after a period of 6 hours the whole is buffered to a pH value of 5.0 with about 5% of sodium bicarbonate in a number of portions. Total treatment time is about 8 to 10 hours. Then 1% of persulfuric acid/sulfite is added and the pH value of the liquor is corrected again to 5.0 after one hour. After having been kept on the horse overnight the hides are fatliquored with 2 to 5% or pure fat in the form of a commercial cationic fatliquor in a 100% liquor at 50° C. Drying, sawdusting and staking are carried out as usual.

Leather prepared in this way is white, has a shrinkage temperature of 88° C, is full and supple in handle and contains the aluminum tan including the acrylic acid in a form incapable of being be washed out.

EXAMPLE 2

Hexacrylato-hexaquo-dialuminum-monochromic chloride having the formula:

$$[Al_2Cr(H_2C{=}CH{-}COO)_6(H_2O)_6Cl_3.$$

A solution of 144 parts of acrylic acid and 106 parts of sodium carbonate in 4,800 parts of water is added to a solution of 161 parts of aluminum chloride ($AlCl_3{\cdot}6H_2O$) and 89 parts of chromic chloride ($CrCl_3{\cdot}6H_2O$) in 200 parts of water while stirring. The aged solution is spray-dried.

A white-green powder is obtained which dissolves well in water with a green color. In addition to sodium chloride and sodium acrylate it contains a salt having the formula:

$$[Al_2Cr(H_2C{=}CH{-}COO)_6(H_2O)_6Cl_3.$$

It may be used as in Example 1 for tanning, with or without pretreatment with formaldehyde. Leather is obtained which withstands the boiling test, has a pale blue color and contains aluminum and acrylic acid radicals in a form incapable of being washed out.

EXAMPLE 3

μ-tetracrylato-μ-dihydroxo-hexaquo-dichromic-monoaluminum-chloride having the formula:

$$[Cr_2Al(H_2C{=}CH{-}COO)_4(OH)_2(H_2O)_6]Cl_3.$$

A solution of 106 parts of sodium carbonate in 1,000 parts of water is added to a solution of 178 parts of chromic chloride ($CrCl_3{\cdot}6H_2O$) and 80 parts of aluminum chloride ($AlCl_3{\cdot}6H_2O$) in 200 parts of water

while stirring and the stirring is continued until the solution is clear. Then 96 parts of monomeric acrylic acid is added. The aged solution is spray-dried.

A green powder is obtained which dissolves in water with a blue color. In addition to sodium chloride it contains a salt having the formula:

$$[Cr_2Al(H_2C{=}CH{-}COO)_4(OH)_2(H_2O)_6]Cl_3.$$

It may be used as in Example 1 for tanning with or without pretreatment with formaldehyde. A grey leather is obtained which contains chromium and aluminum as well as the acrylic acid radicals present in a form incapable of being washed out.

EXAMPLE 4

μ-hexacrylato-hexaquo-trialuminum chloride having the formula:

$$[Al_3(H_2C{=}CH{-}COO)_6(H_2O)_6Cl_3.$$

86.5 parts of monomeric acrylic acid is added to a solution of 136 parts of a commercial 66% basic aluminum chloride ($[Al(OH)_2]Cl+2NaCl$) having a content of 22% Al_2O_3 in 300 parts of water and the whole is made up to 1000 parts with water. The aged solution is spray-dried.

A white powder is obtained which gives a colorless solution in water. It may be used for tanning as in Example 1.

EXAMPLE 1

μ-diacrylato-μ-tetrahydroxo-hexaquo-trialuminum chloride having the formula:

$$[Al_3(H_2C{=}CH{-}COO)_2(OH)_4(H_2O)_6]Cl_3$$

28.8 parts of monomeric acrylic acid is added to a solution of 136 parts of a commercial 66% basic aluminum chloride ($[Al(OH)_2]_{Cl}+2NaCl$) having a content of 22% of Al_2O_3 in 300 parts of water and the whole is made up to 1000 parts with water. The aged solution is spray-dried.

A white powder is obtained which gives a colorless solution in water. It may be used as in Example 1 for tanning pelts or after-tanning chrome leather.

EXAMPLE 6

μ-triacrylato-μ-trihydroxo-hexaquo-dialuminum-monochromic chloride having the formula:

$$[Al_2Cr(H_2C{=}CH{-}COO)_3(OH)_3(H_2O)_6]Cl_3.$$

A mixture of 43.2 parts of monomeric acrylic acid and 33.6 parts of sodium bicarbonate in 500 parts of water is added to a solution of 90.4 parts of a commercial 66% basic aluminum chloride ($[Al(OH)_2]Cl+2NaCl$) having a content of 22% of Al_2O_3 and 53.3 parts of chromic chloride ($CrCl_3{\cdot}6H_2O$) in 300 parts of water and the whole is made up to 1000 parts with water. A blue violet solution is obtained. By spray-drying a green salt is formed which dissolves in water with a green color. It contains sodium chloride as well as the salt according to the invention.

EXAMPLE 7

μ-hexacrylato-hexaquo-monoaluminum-dichromic chloride having the formula:

$$[AlCr_2(H_2C{=}CH{-}COO)_6(H_2O)_6Cl_3.$$

A mixture of 86.5 parts of monomeric acrylic acid and 101 parts of sodium bicarbonate in 500 parts of water is added to a solution of 48.2 parts of aluminum chloride ($AlCl_3{\cdot}6H_2O$) and 106.6 parts of chromic chloride ($CrCl_3{\cdot}6H_2O$) in 300 parts of water, and the whole is made up to 1,000 parts with water. A red violet solution is obtained which changes to green in a few weeks. By spray-drying the red violet solution a green salt is obtained which dissolves in water to give a green solution. It contains sodium chloride in addition to the salt according to the invention.

EXAMPLE 8

μ-diacrylato-μ-tetrahydroxo-hexaquo-monoaluminum-dichromic chloride having the formula:

$$[AlCr_2(H_2C{=}CH{-}COO)_2(OH)_4(H_2O)_6]Cl_3.$$

A mixture of 28.8 parts of monomeric acrylic acid and 67.0 parts of sodium bicarbonate in 500 parts of water is added to a solution of 45.2 parts of a commercial 66% basic aluminum chloride ($[Al(OH)_2]Cl$ + 2NaCl) having an Al_2O_3 content of 22% and 106.6 parts of chromic chloride ($CrCl_3{\cdot}6H_2O$) in 300 parts of water and the whole is made up to 1000 parts with water. An ink blue solution is obtained. By spray-drying a blue green salt is obtained which gives a dark blue solution in water. It may be used for tanning as in Example 1.

We claim:

1. A complex trinuclear metal salt whose cation has the formula

$$[M_a^1 M_{(3-a)}^2 R_m(OH)_{(6-m)}(H_2O)_6b]^{(+X+X+)}$$

where M^1 denotes aluminum and M^2 denotes trivalent chromium as the central atoms, R denotes the radical of acrylic acid twice combined between two metal atoms, a denotes an integer from 1 to 3 and m denotes an integer from 2 to 6 and which contains monovalent anions which do not make the complex metal salt insoluble, which anions are selected from the group consisting of chloride, bromide, iodide, perchlorate, nitrate, formate, acetate and propionate ions.

2. A complex trinuclear metal salt as claimed in claim 1 in which a in the formula of the cation denotes one of the integers 1 and 2.

3. A complex trinuclear metal salt as claimed in claim 2 which contains chloride ions as the monovalent anions.

4. A complex trinuclear metal salt whose cation has the formula

$$[Al_3R_m(OH)_{(6-m)}(H_2O)_6]^{(+X+X+)}$$

R denotes the radical of acrylic acid combined twice between two metal atoms, and m denotes one of the integers from 2 to 6, and which contains anions which do not make the complex metal salt insoluble, which anions are selected from the group consisting of chloride, bromide, iodide, perchlorate, nitrate, formate, acetate and propionate ions.

5. A complex trinuclear metal salt as claimed in claim 4 which contains chloride ions as the monovalent anions.

6. $[Al_2Cr(H_2C{=}CH{-}COO)_6(H_2O)_6]Cl_3$.

7. $[AlCr_2(H_2C{=}CH{-}COO)_4(OH)_2(H_2O)_6]Cl_3$.

8. $[Al_2Cr(H_2C{=}CH{-}COO)_3(OH)_3(_2O)_6]Cl_3$.

9. $[AlCr_2(H_2C{=}CH{-}COO)_6(H_2O)_6]Cl_3$.
10. $[AlCr_2(H_2C{=}CH{-}COO)_2(OH)_4(H_2O)_6]Cl_3$.
11. $[Al_3(H_2C{=}CH{-}COO)_3(OH)_3(H_2O)_6]Cl_3$.
12. $[Al_3(H_2C{=}CH{-}COO)_2(OH)_4(H_2O)_6]Cl_3$.

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PO-1050
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,714,211 Dated January 30, 1973

Inventor(s) Hans Erdmann and Franz Friedrich Miller

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Cover page, left-hand column, insert
-- [30] Foreign Application Priority Data
September 5, 1969 Germany . . . P 19 45 006.7 --.

Column 2, line 12, "$[Al_3R_4(OH)(H_2O)_6]A_3$" should read
-- $[Al_3R_4(OH)_2(H_2O)_6]A_3$ --.

Column 5, line 39, "$([Al(OH)_2]Cl+2NaCl)$" should read
-- $([Al(OH)_2]Cl + 2NaCl)$ --.

Column 6, line 35, claim 1, "$[M_a^1M_{(3-a)}^2R_m(OH)_{(6-m)}(H_2O)_6b]^{(+x+x+)}$" should read -- $[Ma^1M^2(3-a)R_m(OH)_{(6-m)}(H_2O)_6b]$ (+)(+)(+) --.

Signed and sealed this 9th day of October 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents