United States Patent [19]

Erdmann et al.

[11] **3,792,976**

[45] **Feb. 19, 1974**

[54] **ALUMINUM-CHROME ACRYLIC ACID COMPLEX TANNAGE AND LEATHER ALUMINUM OR**

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[22] Filed: **Nov. 4, 1971**

[21] Appl. No.: **195,871**

Related U.S. Application Data

[62] Division of Ser. No. 069,461, Sept. 3, 1970, Pat. No. 3,714,211.

[30] **Foreign Application Priority Data**

Sept. 5, 1969 Germany 1945006

[52] **U.S. Cl.** **8/94.26,** 8/94.27, 8/94.29

[51] **Int. Cl.** **C14c 3/02**

[58] **Field of Search** 8/94.27, 94.29, 94.26, 94.21

[56] **References Cited**

UNITED STATES PATENTS

2,220,867	11/1940	Kirk	8/94.29 X
2,327,815	8/1943	Niedercorn	8/94.29 X
2,942,930	6/1960	Luvisi et al.	8/94.29
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Primary Examiner—Donald Levy

[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 of acrylic acid and a method of tanning using these metal salts.

6 Claims, No Drawings

ALUMINUM-CHROME ACRYLIC ACID COMPLEX TANNAGE AND LEATHER ALUMINUM OR

RELATED APPLICATION

This application is a division of our application Ser. No. 69,461, filed Sept. 3, 1970, now U.S. Pat. No. 3,714,211.

The present invention relates to new salts which contain aluminum or aluminum and trivalent chrominum 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:

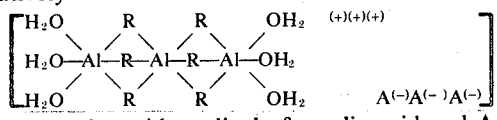
$$[M_a^1\ M_{(3-2)}^2\ R_m\ (OH)_{(6-m)}(H_2O)_3]^{(+)(+)(+)}$$

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:

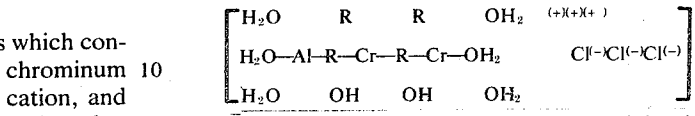


R denotes the acido radical of acrylic acid and A denotes a monovalent anion from the group given above.

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-mono-chromic or monoaluminum-dichromic complex salts having the same structure:

$[Al_3R_5(OH)(H_2O)_6]A_3$ — $[Al_3R_4(OH)_2(H_2O)_6]A_3$

$[Al_3R_3(OH)_3(H_2O)_6]A_3$ — $[Al_3R_2(OH)_4(H_2O)_6]A_3$

$[Al_2CrR_6(H_2O)_6]A_3$ — $[Al_2CrR_5(OH)(H_2O)_6]A_3$

$[Al_2CrR_4(OH)_2(H_2O)_6]A_3$ — $[Al_2CrR_3(OH)_3(H_2O)_6]A_3$

$[Al_2CrR_2(OH)_4(H_2O)_6]A_3$ — $[AlCr_2R_6(H_2O)_6]A_3$

$[AlCr_2R_5(OH)(H_2O)_6]A_3$ — $[AlCr_2R_4(OH)_2(H_2O)_6]A_3$

$[AlCr_2R_3(OH)_3(H_2O)_6]A_3$ — $[AlCr_2R_2(OH)_4(H_2O)_6]A_3$.

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 formulae 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 those of urea, cyclic urea derivatives, melamine and dicyanodiamide. It has proved suitable to use the aldehydes in amounts of from 0.5 to 3 percent, preferably 1 to 1.5 percent, 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 percent 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 99°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 percent 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 percent basic aluminum chloride (22 percent 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 percent of aqueous liquor containing 10 percent of sodium chloride and 3 percent of 30 percent aqueous formaldehyde solution. Thirty minutes later 15 percent of triacrylato-trihydroxotrialuminum 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 percent of sodium bicarbonate in a number of portions. Total treatment time is about 8 to 10 hours. Then 1 percent of persulfuric acid/sulfite is added and the pH value of the liquor is corrected again to 5.0 after 1 hour. After having been kept on the horse overnight the hides are fatliquored with 2 to 5 percent or pure fat in the form of a commercial cationic fatliquor in a 100 percent 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:

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

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:

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

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 gray 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:

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

86.5 parts of monomeric acrylic acid is added to a solution of 136 parts of a commercial 66 percent basic aluminum chloride ($[Al(OH)_2]Cl+2NaCl$) having a content of 22 percent Al_2O_3 in 300 parts of water and the whole is made up to 1,000 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 5

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

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

28.9 parts of monomeric acrylic acid is added to a solution of 136 parts of a commercial 66 percent basic aluminum chloride ($[Al(OH)_2]Cl+2NaCl$) having a content of 22 percent of Al_2O_3 in 300 parts of water and the whole is made up to 1,000 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 percent basic aluminum chloride ($[Al(OH)_2]Cl+2NaCl$) having a content of 22 percent 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 1,000 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:

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

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 percent basic aluminum chloride ($[Al(OH)_2]Cl + 2NaCl$) having an Al_2O_3 content of 22 percent 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. 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 process for tanning pelts wherein a complex trinuclear metal salt whose cations have the formula

$$[M_a^1 M_{(3-a)}^2 R_m (OH)_{(6-m)}(H_2O)_6] (^+)(^+)(^+)$$

where M^1 denotes aluminum and M^2 denotes trivalent chromium as central atoms, R denotes the radical of acrylic acid which is 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 render the complex metal salt insoluble, and which are selected from the group consisting of chloride, bromide, iodide, perchlorate, nitrate, formate, acetate and propionate ions, is allowed to act on the pelts, said pelts having been bated, delimed and pretreated with an aldehyde or a substance yielding an aldehyde, and tanning is carried to completion under the conditions conventionally employed with other aluminum tans.

2. A tanning process as claimed in claim **1** wherein, following the treatment, the acrylato radicals contained in the complex salt are homopolymerized.

3. Leather which has been obtained from a pelt which has been tanned with a complex trinuclear metal salt whose cations have the formula:

$$[M_a^1 M_{(3-a)}^2 R_m (OH)_{(6-m)} (H_2O)_6] (^+)(^+)(^+)$$

where M^1 denotes aluminum and M^2 denotes trivalent chromium as 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 in water and are selected from the group consisting of chloride, bromide, iodide, perchlorate, nitrate, formate, acetate and propionate ions.

4. Leather as claimed in claim **3** wherein *a* denotes one of the integers 1 or 2.

5. Leather as claimed in claim **4** wherein said monovalent anions are chloride ions.

6. Leather as claimed in claim **3** wherein said monovalent anions are chloride ions.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,792,976 Dated February 19, 1974

Inventor(s) Hans Erdmann & 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:

First page, left-hand column, lines 1-3, "ALUMINUM-CHROME ACRYLIC ACID COMPLEX TANNAGE AND LEATHER ALUMINUM OR" should read -- ALUMINUM OR ALUMINUM-CHROME ACRYLIC ACID COMPLEX TANNAGE AND LEATHER --.

First page, left-hand column, fifteenth line, "1945006" should read -- P 19 45 006.7 --.

Column 1, lines 1-2, "ALUMINUM-CHROME ACRYLIC ACID COMPLEX TANNAGE AND LEATHER ALUMINUM OR" should read -- ALUMINUM OR ALUMINUM-CHROME ACRYLIC ACID COMPLEX TANNAGE AND LEATHER --.

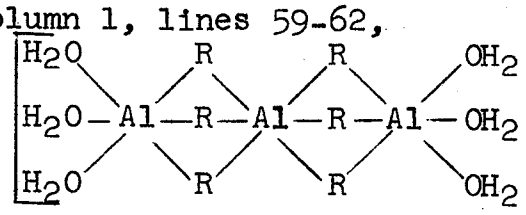
Column 1, line 10, "chrominum" should read -- chromium --.

Column 1, lines 36-37, "$\left[M_a{}^1M_{(3-2)}{}^2R_m(OH)_{(6-m)}(H_2O)_3\right](+)(+)(+)$"

should read -- $\left[M_{\underline{a}}{}^1M^2{}_{(3-\underline{a})}R_{\underline{m}}(OH)_{(6-\underline{m})}(H_2O)_3\right]$ $(+)(+)(+)$ --.

Column 1, lines 59-62,

"



$(+)(+)(+)$

$A(-)_A(-)_A(-)$ "

should read

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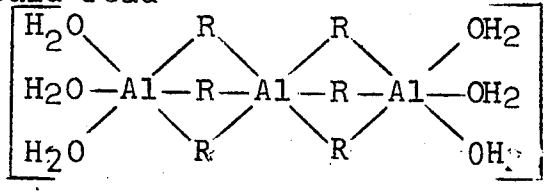


$(+)(+)(+)$

$A(-)_A(-)_A(-)$ --.

UNITED STATES PATENT OFFICE

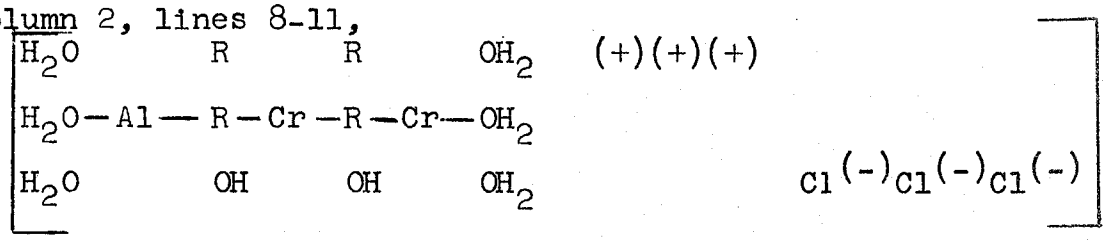
CERTIFICATE OF CORRECTION

Patent No. 3,792,976 Dated February 19, 1974

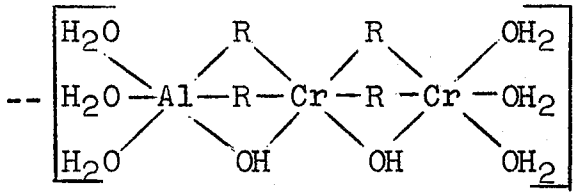
Inventor(s) Hans Erdmann & Franz Friedrich Miller

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

Column 2, lines 8-11,

"  (+)(+)(+) $Cl^{(-)}Cl^{(-)}Cl^{(-)}$

should read

--  (+)(+)(+) $Cl^{(-)}Cl^{(-)}Cl^{(-)}$

Column 3, line 46, "99 C." should read --890 C. --.

Column 6, line 32-33, " $\left[M_a{}^1M_{(3-a)}{}^2R_m(OH)_{(6-m)}(H_2O)_6\right]$ (+)(+)(+)"

should read -- $\left[M_{\underline{a}}{}^1M^2{}_{(3-\underline{a})}R_{\underline{m}}(OH)_{(6-\underline{m})}(H_2O)_6\right]$ (+)(+)(+)

Column 6, lines 54-55, " $\left[M_a{}^1M_{(3-a)}{}^2R_m(OH)_{(6-m)}(H_2O)_6\right]$ (+)(+)(+)"

should read -- $\left[M_{\underline{a}}{}^1M^2{}_{(3-\underline{a})}R_{\underline{m}}(OH)_{(6-\underline{m})}(H_2O)_6\right]$ (+)(+)(+)

Signed and Sealed this

Eighteenth Day of January 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks