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## ANTIPERSPIRANT COMPOSITIONS CONTAINING ALUMINUM CHELATES OF HYDROXY CARBOXYLIC ACIDS

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No Drawing. Continuation-in-part of applications Ser. No. 236,168, Nov. 7, 1962, Ser. No. 255,218, Jan. 31, 1963, and Ser. No. 668,886, July 1, 1957. This application Apr. 25, 1966, Ser. No. 544,833  
Int. Cl. A61k 1/00

U.S. Cl. 424—68

13 Claims

### ABSTRACT OF THE DISCLOSURE

Antiperspirant and antacid aluminum chelates and methods for preparing the same in which an aluminum compound selected from the group consisting of alkali metal aluminates and aluminum chlorhydroxy complexes is chelated with water and alcohol soluble hydroxy carboxylic acids.

This application is a continuation-in-part of U.S. patent application Ser. No. 668,886 filed July 1, 1957 by Andrew M. Rubino for Anionic Antiperspirant.

This application is also a continuation-in-part of U.S. patent application Ser. No. 236,168 filed Nov. 7, 1962 in the names of Andrew M. Rubino and James J. Martin, Jr. for Alkaline Earth Metal Salts of Aluminum Hydroxy Aliphatic Acid Chelates and Antacid Compositions Containing the Same.

This application is also a continuation-in-part of U.S. patent application Ser. No. 255,218 filed Jan. 31, 1963 in the name of Andrew M. Rubino for Aluminum Chelates and Compositions Containing the Same.

The above noted three applications are now abandoned.

This invention relates to chelates of hydroxy carboxylic acids and methods for preparing the same.

The compounds of this invention have particular utility in antacid compositions, in antiperspirant compositions, and as buffers.

Aluminum chlorhydroxy complexes in liquid form have proven very successful as antiperspirants. This invention makes possible and practicable an antiperspirant that may be made into stick form in effective concentration corresponding to as much as 24% or so of the antiperspirant compound, that is soluble in alcohol or methanol, is not subject to precipitation of aluminum by alkali at any pH up to 9 and that may be used, therefore, at such pH as to eliminate any acidic action of the antiperspirant on fabrics or the skin, is not precipitable by soaps in alcoholic solution and so may be used in a soap stick without separation of aluminum soap.

Antacid preparations are now quite generally employed for the treatment of peptic ulcers, gastric hyperacidity and dyspepsia. Gwilt, Livingstone, and Robertson in the Journal of Pharmacy and Pharmacology, X, No. 12, 770-775 (1958), describe the characteristics of an ideal antacid. They point out that it should show its maximum neutralizing effect in the shortest possible time, that it should neutralize an adequate amount of gastric hydrochloric acid and maintain its action during the normal period of gastric digestion, that any excess however great beyond the amount required to neutralize free gastric acid should not cause alkalization, that it should raise the pH of the gastric contents to a level at which pepsin activity is reduced significantly but not totally inhibited, that adequate and repeated doses should be palatable to the hyperacid patient, and that its use should not lead to constipating or other side effects such as gastric irritation. In ad-

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dition to these factors, the antacid composition should be inexpensive, and it should not deteriorate significantly in any respect on aging. These workers summarize the various statements in the literature as to the pH ranges desirable for the ideal antacid, and conclude that a pH within the range from about 3 to about 5 is apparently the optimum, to ensure adequate relief from hyperacidity, particularly if an ulcer site is present, and at the same time permit sufficient residual pepsin activity to avoid secondary digestive disturbances.

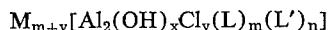
Edwards in The Chemist and Druggist, Dec. 14, 1957, page 647, also discusses the properties of an ideal antacid, and suggests that the nearest approach to the ideal attained as of that date was wet activated alumina gel. Dr. Edwards' views of the properties of the ideal antacid are in substantial agreement with those expressed by Gwilt et al.

Liquid aluminum hydroxide gel closely approaches the ideal for an antacid, but its liquid form makes it inconvenient to use, especially in the case of ambulatory patients. The liquid gel is quite rapid in its action, and gives a prolonged antacid effect in the optimum pH range. It is not significantly affected in its antacid properties by pepsin, and it also does not significantly lose its antacid characteristics on aging. However, as Edwards and others have pointed out, it may have a mildly constipating effect, which many have sought to remedy by combining it with other ingredients such as magnesium hydroxide or carbonate.

The advantages of the dried gel are obvious. However, the obvious material, dried aluminum hydroxide gel, is actually far from an ideal antacid. It exhibits a lag in its rate of reaction with stomach acids. It does not give prolonged antacid activity in the optimum pH range, and its antacid properties are severely affected by pepsin. Also, its antacid activity is less than that of the liquid gel, being decreased by the drying, and the reduced activity decreases further with aging. These disadvantages have been noted by Gwilt et al. and other workers in this field.

A number of combinations incorporating aluminum hydroxide gels have been proposed, in which the antacid activity is enhanced by incorporating therewith another compound, such as magnesium carbonate, magnesium silicate, calcium carbonate, and the like. All of these compositions suffer from a major drawback inherent in the use of aluminum hydroxide gel, its relative insolubility in the stomach fluids. Antacid action is not demonstrated immediately, but instead there is a certain time interval before a sufficient amount of the antacid composition has been dissolved to affect the pH of the stomach. This drawback prevents such compositions from showing their maximum neutralizing effect in the shortest possible time, although they are quite effective in maintaining an optimum pH over a long period of time.

The aluminum chelates of the present invention are formed from organic acids having a hydroxyl group alpha and/or beta to the carboxylic acid radical selected from the group consisting of lactic, citric, tartaric, glycolic, gluconic, trihydroxy glutaric, citryl trigluconic, citryl monogluconic, citryl digluconic, malic, tetrahydroxy adipic, and citramalic acids, and mixtures thereof, in which the chelate has the following formula:



where M represents a non-toxic cation such as sodium, potassium, lithium, magnesium, calcium, zinc, zirconium, aluminum, or ammonium, or mixtures of the foregoing cations, and L and L' are the two forms of the same ligand derived from the hydroxy carboxylic acid. L and L' are at least bidentate, and have a valence of between -1 to -4; L corresponds to that form of the acid in which both the carboxyl and hydroxyl groups have been

neutralized, L' corresponds to that form of the acid in which only the carboxyl groups have been neutralized, and whose hydroxyl group is coordinated to an aluminum atom; where  $y$ ,  $m$ ,  $n$ , and  $x$  are numbers whose sum is such as to balance the positive valences of the cation M, and aluminum;  $m+y$  is the total number of gram atoms of the cation M; and  $m+n$  is the total number of gram molecular weights of alpha- or beta-hydroxy aliphatic carboxylic acid. It is to be understood that in some chelates, only L is present; in other chelates only L' is present; and in still other chelates both L and L' are present.

The numbers representing  $y$ ,  $m$ ,  $n$ , and  $x$  need not be integers, but may be fractional quantities.

In the case of bidentate chelation with such ligands as glycolates, lactates, gluconates, and malates, the value of  $m+n$  will range from 2 to 6,  $x$  from 0 to 4,  $y$  from 0 to 1,  $m$  from 0 to 6, and  $n$  from 0 to 6.

In the case of tridentate chelation with such ligands as gluconates, citrates, tartrates, malates, citryl trigluconates, citryl digluconates, citryl monogluconates, citramalates, trihydroxyglutarates, and tetrahydroxy adipates; the value of  $m+n$  will range from 2 to 4,  $x$  from 0 to 2,  $y$  from 0 to 1,  $m$  from 0 to 4, and  $n$  from 0 to 4.

In the case of tetridentate chelation with such ligands as gluconates, citrates, tartrates, citryl gluconates, citryl digluconates, citryl monogluconates, citramalates, trihydroxyglutarates, and tetrahydroxy adipates; the value of  $m+n$  will range from 2 to 3,  $x$  from 0 to 2,  $y$  from 0 to 1,  $m$  from 0 to 3, and  $n$  from 0 to 3.

In the case of the use of alkali metal aluminates as the aluminum source, namely when  $y$  is 0 (chlorine atoms being absent), the total number of gram atoms of cation or cations will be represented as the sum of  $m+n$ , and the chelate will have the following empirical formula:



where L and L' are the two forms of the same ligand derived from the hydroxy carboxylic acid. L and L' are at least bidentate and have a valence between -1 and -4; L corresponds to that form of the acid in which both the carboxyl and hydroxyl groups have been neutralized, L' corresponds to that form of the acid in which only the carboxyl group has been neutralized, and whose hydroxyl group is coordinated to an aluminum atom; where  $m$ ,  $n$ , and  $x$  are numbers whose sum is such as to balance the positive valences of the cation M, and aluminum,  $m+n$  is the total number of gram atoms of the cation M, M representing a non-toxic cation such as sodium, potassium, lithium, magnesium, calcium, zinc, zirconium, aluminum, or ammonium, or mixtures of the foregoing cations, and  $m+n$  is the total number of gram molecular weights of alpha- or beta-hydroxy aliphatic carboxylic acid. It is to be understood that in some chelates, only L is present; in other chelates only L' is present; and in still other chelates both L and L' are present.

The numbers representing  $m$ ,  $n$ , and  $x$  need not be integers, but may be fractional quantities.

In the case of bidentate chelation with such ligands as glycolates, lactates, gluconates, and malates; the value of  $m+n$  will range from 2 to 6, and  $x$  from 0 to 6.

In the case of tridentate chelation with such ligands as gluconates, citrates, malates, tartrates, citryl trigluconates, citryl digluconates, citryl monogluconates, citramalates, trihydroxyglutarates, and tetrahydroxy adipates; the value of  $m+n$  will range from 2 to 4, and  $x$  from 0 to 4.

In the case of tetridentate chelation with such ligands as gluconates, citrates, tartrates, citryl trigluconates, citryl digluconates, citryl monogluconates, citramalates, trihydroxyglutarates, and tetrahydroxy adipates; the value of  $m+n$  will range from 2 to 3 and  $x$  from 0 to 4.

It will be evident from the above that  $m$  represents the number of gram molecular weights of hydroxy carboxylic acid in which the hydrogen of the hydroxy group is re-

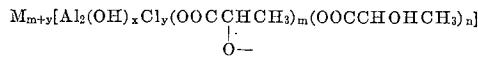
placed by cation M, and  $n$  the number of gram molecular weights of hydroxy carboxylic acid in which the hydrogen of the hydroxy group has not been neutralized and may be shown in its original position or outside the brackets as H+.

In the above formulae, the remainder of the molecule enclosed within the brackets, other than the cation M, is anionic. Thus, the aluminum is entirely in the anionic portion of the molecule, except in those compounds where the aluminum is in both the cationic and anionic portions of the molecule.

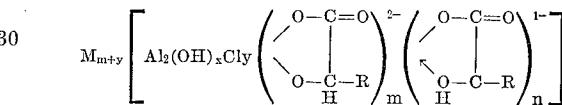
The value of  $y$  in the above formulae can be widely varied within the limits indicated. Particularly satisfactory complexes are obtained when the proportion of aluminum to chlorine in the complex is approximately 1.5 to 2.5:1.

It is also possible to formulate complexes in which  $y$  is 0, i.e., no chlorine is present. Such complexes are also quite satisfactory antacids and antiperspirants.

As an example, when the hydroxy carboxylic acid is lactic acid, the formula takes on the specific representation:

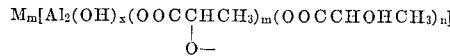


Alternatively, since the term chelate denotes the combination of a metal with a ligand in a ring structure, the following empirical formula can be depicted as representative:

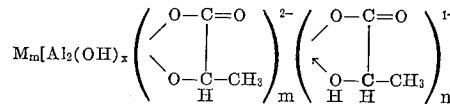


(The ring structures are understood to include aluminum or to be bonded directly to the aluminum atom within the brackets) in which  $m$ ,  $n$ ,  $y$ ,  $x$ , and M are the same as above. The total of  $m+n$  is within the range of 2 to 6, and  $x$  is  $6-(m+n)$ .

A complex free from chlorine and incorporating lactic acid has the formula:



or



These complexes are extremely water-soluble and, in aqueous solution, are in equilibrium with only a very small concentration of aluminum ion. Thus, aluminum is available by ionization and as the chelate for antacid or antiperspirant activity, which is desirable, but an insufficient amount of aluminum ion is present to precipitate in the form, for example, of aluminum hydroxide, or aluminum soap. The amount of aluminum ion in solution is so small that the solubility products of aluminum hydroxide and aluminum soaps are not exceeded. Naturally, these properties are quite advantageous. Indeed, the solubility of the anionic portion including the aluminum ion is so high, that each of the aforementioned metal salts are quite water-soluble, corresponding in solubility characteristics to calcium nitrate or calcium chloride, rather than to calcium hydroxide or magnesium hydroxide.

As the hydroxy carboxylic acid, any aliphatic carboxylic acid in which the hydroxyl group is alpha or beta to the carboxylic acid group can be employed. The acid may contain a plurality of hydroxyl groups, provided at least one is in the alpha or beta position, and the acid may also include a plurality of carboxylic acid groups, provided again that at least one hydroxyl group is alpha or beta to at least one of the carboxylic acid groups. Mixtures of such acids can be used. Typical hydroxy aliphatic acids that can be employed include lactic acid,

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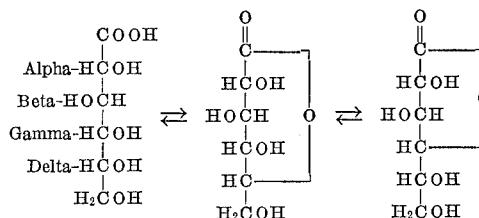
glycolic acid, gluconic acid, trihydroxy glutaric acid, citryl trigluconic acid, citryl monogluconic acid, citryl di-gluconic acid, tartaric acid, malic acid, citric acid, tetra-hydroxy adipic acid, and citramalic acid.

It is important to note that the hydroxy carboxylic acid is, in each instance, aluminum-chelating and non-toxic under the conditions of use, as well as water-soluble, and soluble or miscible in alcohol, and by "alcohol" is meant both monohydroxy and polyhydroxy alcohols.

These formulae postulate the existence of these chelate compounds as monomers, but also include polymers. It is emphasized that the formulae are empirical. It is well known that aluminum basic compounds containing OH groups in the molecule such as aluminum hydroxide exist as polymers, in the solid state as well as in aqueous systems, Colloid Chemistry, Arthur W. Thomas, 1st edition, 1934, McGraw-Hill Book Co., New York, pp. 145-149 et seq., and The Chemistry of the Coordination Compounds, John C. Bailar, 1956, Reinhold Publishing Company, New York.

Gluconic acid of commerce is actually D-gluconic acid. Solutions thereof may be prepared by the dissolution of glucono-delta-lactone in water.

In aqueous systems, gluconic acid is in equilibrium with gamma- and delta-gluconolactones, viz:



The positions of the secondary alcohol groups are systematized in the art for convenience in elaborating the lactone equilibration phenomena, as well as to depict more clearly, the possible coordination sites of gluconate ligands. Customarily, gluconates are believed to function as bidentate, tridentate and possibly tetradentate ligands, although more often than not, physicochemical data suggest the presence of tridentation between gluconate ligands and numerous metals, among which are included aluminum, iron, chromium, etc.

The oxygens of the secondary hydroxyl groups as well as the carboxylate oxygen are believed to participate in coordinate bonding with metals. Where a multiplicity of such bonds occurs in one molecule, polydentation or chelation thereby results.

Dentation increases as a function of the pH in numerous metal systems and is in part determined by the nature of the metal ion, as well as other parameters.

The state of the art, insofar as the ability to characterize such polydentate chelates, is such that it is rarely known with certainty exactly how many and which secondary hydroxyl groups participate with the carboxylate oxygen in chelate formation in the many metal systems.

It may thus be possible, depending on reaction conditions, to chelate more than one metal atom per mole of ligand. Conversely 2 moles of ligand may chelate with 1 gram atom of metal, with varying degrees of dentation attributable to the gluconate ligand. For example, one gluconate ligand may be bidentate; the other may be tridentate and both may conceivably be chelated to the same aluminum atom.

In gluconate systems, of importance is the theoretical consideration that secondary hydroxyl coordination to metal ions may be envisioned without the necessity for prior loss or neutralization of the hydrogen on such hydroxyl groups, although hydrogen may be shown outside the brackets to denote its liability or potential loss.

The foregoing is by way of illustrating the relative nature of chelation structures in connection with ligands which are capable of demonstrating greater than bidentate

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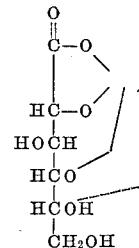
chelation, among which are numbered for example, gluconates, citrates and tartrates.

It is one thing to be aware of the theoretical coordinating capacity of a given ligand; it is quite another to postulate even with moderate certainty, its particular disposition in a given metal complex system.

Gluconate-chelate structures herein postulated are done so with the aforementioned in mind.

Where hydroxy containing complexes are shown, as for example, potassium or sodium aluminum hydroxy gluconates, citrates or tartrates, it is unknown whether or not the ligand displaces such hydroxy group by virtue of substituting one of its "reserve" coordination sites to form a ring or chelate structure with aluminum—which structure is considered theoretically much more stable than the so-called "simple" covalently bonded hydroxide to aluminum bond.

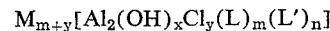
Tridentate gluconate ligand or possible tetradentate ligand structures.



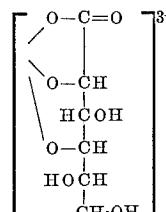
NOTE: The dotted line illustrates the possible contribution of the delta hydroxy (secondary hydroxy group) to chelation structures. This may occur in place of, or in addition, to gamma hydroxy coordination to the central metal ion (i.e., aluminum).

Although the gamma hydroxy hydrogen is not shown in the depicted structure above, its absence being ascribable to either conversion to water, by neutralization, or simply by way of illustrating its lability by positioning it outside the brackets with the secondary metals (e.g., alkali metals, alkaline earth metals, zinc, zirconium, cationic aluminum, etc.), it is theoretically not mandatory to show its absence in order to justify the alcoholic or hydroxy group's coordination and chelation to the central metal ion, i.e., aluminum.

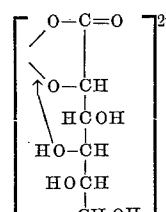
The aluminum chelates of gluconic acid follow the formula:



with M representing a non-toxic cation such as sodium, potassium, lithium, magnesium, calcium, zinc, zirconium, aluminum, or ammonium, or mixtures of the foregoing cations; where L and L' are the two forms of the tridentate ligand, and have a valence ranging between -2 to -3 with L corresponding to the following form:

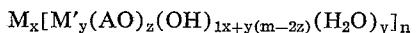


in which the carboxyl and both the hydroxyl groups have been neutralized, and L' corresponding to the following form:

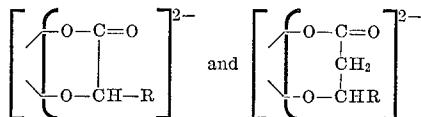


in which the carboxyl and only one of the coordinated hydroxyl groups has been neutralized; where  $y$ ,  $m$ ,  $n$ , and  $x$  are numbers whose sum is such as to balance the positive valences of the cation  $M$ , and aluminum;  $m+y$  is the total number of gram atoms of the cation  $M$ ; and  $m+n$  is the total number of gram molecular weights of hydroxy carboxylic acid; and wherein the value of  $m+n$  will range from 2 to 4,  $x$  from 0 to 2,  $y$  from 0 to 1,  $m$  from 0 to 4, and  $n$  from 0 to 4.

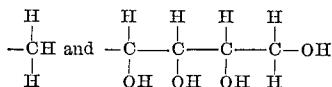
In particular, many chelates of the present invention can be written as:



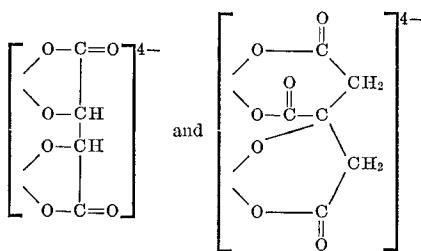
wherein  $M$  is selected from the group consisting of magnesium, aluminum, sodium, potassium, the ammonium radical, calcium, zinc, zirconium, and iron, with the magnesium, aluminum, sodium, potassium, the ammonium radical, calcium, zinc, bismuth and zirconium being preferred, and  $M'$  is selected from the group consisting of magnesium, aluminum, and iron, with aluminum being preferred,  $AO$  is selected from the group consisting of the bidentate ions formed from the monocarboxylic alpha-hydroxy acids and the monocarboxylic beta-hydroxy acids of the formula:



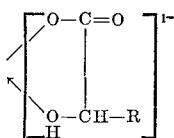
in which  $R$  is one of the groups



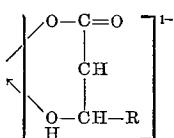
and the tetradentate ions formed from tartaric and citric acids of the respective formulae:



In place of  $AO$ , the present invention contemplates the substitution of  $AOH$  in the form of the bidentate ion formed from the monocarboxylic alpha-hydroxy acid of the formula:



and of the monocarboxylic beta-hydroxy acids of the formula:



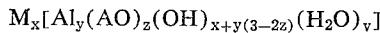
It is seen from the foregoing that the  $AO$  constitutes a bivalent bidentate ion and the  $AOH$  constitutes a univalent bidentate ion.

In the formula for the chelate  $x$  is an integer from 1 to 5, and preferably from 1 to 4 inclusive;  $y$  is unity for bidentate ions and 2 for tetradentate ions;  $z$  is an integer from 1 to 4, and preferably from 1 to 3 inclusive;  $n$  is 2 for bidentate ions when the valency of  $M$  is greater than 1 and is unity in all other cases; 1 is the valency of  $M$

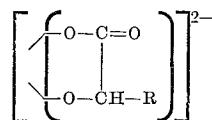
divided by  $n$ ;  $m$  is the valency of  $M'$  and  $v$  is an integer from 0 to 6 inclusive with the proviso that when  $M$  and  $M'$  are the same metal then  $z$  is not less than  $y$ .

As heretofore set forth, the chelates of the present invention comprise polymeric forms, as well as the monomeric form.

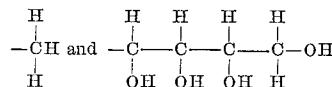
Chelates of the following formula have been prepared:



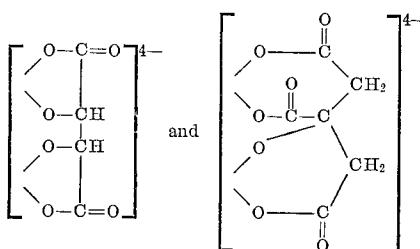
wherein  $M$  is selected from the group consisting of sodium and potassium,  $AO$  is selected from the group consisting of the bidentate ions formed from the monocarboxylic alpha-hydroxy acids of the formula:



in which  $R$  is one of the groups



and the tetradentate ions formed from tartaric and citric acids of the respective formulae:



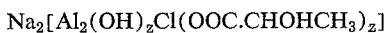
$x$  is an integer from 1 to 5, and preferably from 1 to 4 inclusive;  $y$  is unity for bidentate ions and 2 for tetradentate ions;  $z$  is an integer from 1 to 4, and preferably from 1 to 3 inclusive;  $n$  is 2 for bidentate ions when the valency of  $M$  is greater than 1 and is unity in all other cases; 1 is the valency of  $M$  divided by  $n$ ;  $m$  is the valency of  $M'$  and  $v$  is an integer from 0 to 6 inclusive; and polymeric forms thereof.

In respect to the aluminum antiperspirant aspects of the present invention, the aluminum is contained in the anionic part of the molecule and is chelated by less than the equivalent proportion, by which is meant less than the maximum number of coordinate positions available on the aluminum atom, and ordinarily about half this proportion of lactic or like chelating carboxylic acid. The process of the invention comprises reacting an aluminum compound with the chelating carboxylic acid and establishing the pH of the finished product, by the addition of sodium hydroxide or like alkali, at a level of about 7.5-9 in case the product is to be used in the soap stick type of antiperspirant or at about 3-9, and preferably 4-9, for use in a liquid solution, as in a spray or other conventional type of antiperspirant.

The chelation only to this extent leaves the aluminum active as an antiperspirant, increases the number of equivalents of aluminum for unit weight of the entire antiperspirant and thus makes possible an effective proportion of aluminum for a stick antiperspirant, and, on the other hand, chelates the aluminum to the extent that the product is miscible with alcohol and the aluminum therein is not precipitable by soap. With such a complex, the alcohol content of the antiperspirant stick of desired consistency may be decreased to a desirably low level, as, for example, as little as 30%-40% of the total weight and usually about 35%. Such low proportion of alcohol eliminates or minimizes the irritation caused on certain skins by alcohol of the high concentration otherwise required in stick antiperspirants, decreases the proportion of the

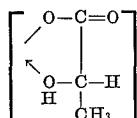
whole antiperspirant composition that evaporates quickly after application, and decreases also the dehydrating effect caused by alcohol of high concentration on the skin.

A representative material that illustrates the class of the antiperspirant is the complex involving the radical of the chelating acid (here lactic) and having the various components in proportions about as shown in the empirical formula

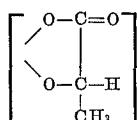


$x$  and  $z$  being numbers whose sum is such, as with the Cl, to balance the positive valences of the sodium and aluminum, that is, 8 in this formula. More specifically,  $z$  represents the number of equivalent weights of the acid chelate (here moles of lactate). Thus  $z$  is a number within the range 2-4 and  $x=7-z$ . The sodium or the other alkali metal content is variable, as in the proportion corresponding to 1-1.6 atoms for 1 Al. The part within the bracket is anionic.

Normally,  $z$  is a number within the range 2-4 and the chelate can be represented as either the  $(\text{OOCCHOHCH}_3)_z$ ,



or  $[\text{OOCCHOHCH}_3]$



according to the number of equivalent weights of sodium or alkali metal.

An alternative but generally less satisfactory antiperspirant, that cannot be dissolved in a stick to the concentration necessary for best results and that we have made, omits the chlorine. A representative product of this modified type corresponds to the composition of about the proportions shown in the empirical formula



Particularly satisfactory results are obtained when the compound reacted with the carboxylic acid is an acidic aluminum hydroxy compound. Thus we use to advantage any one of the aluminum chlorhydroxy complexes at present in use as antiperspirants, as for instance the one of the empirical formula  $\text{Al}_2(\text{OH}_5)\text{Cl}$  or any one in which the proportion of Al:Cl in the complex is about 1.5-2.5:1.

As the aluminum compound for our process of making the less satisfactory product containing no chlorine, we may start with a basic aluminum compound. Examples of such basic compounds that we use are sodium, potassium, and ammonium aluminates. These are understood to contain, when dissolved in water, coordinated hydroxy groups.

The carboxylic acid used to react with the selected aluminum compound is metal chelating, non-toxic under the conditions of use, water and alcohol soluble, and suitably of molecular weight that is relatively low. By "alcohol" as used herein is meant to include both monohydroxy alcohols, and polyhydroxy alcohols, such as glycerol, ethylene glycol, propylene glycol, butylene glycol and solutions of hexitols. Lactic acid meets the requirements and illustrates the class to be chosen. Other hydroxycarboxylic acids that may be used less effectively, as in making sticks of lower aluminum content, are citric, tartaric, and mixtures thereof. Still other hydroxycarboxylic acids that are water or alcohol soluble may be used. Examples of these include glycolic, gluconic, trihydroxy glutaric, citryl trigluconic, citryl monogluconic, citryl digluconic, malic, tetrahydroxy adipic, and citramalic acids, and mixtures thereof.

For stick antiperspirants, amino acids are not recommended.

As to proportions in respect to antiperspirant sticks, we use a balance between the total of basic and acidic groups so as to establish the best pH levels for the different forms of the finished antiperspirant. The proportion of the hydroxycarboxylic acid must be adequate to make the aluminum in the antiperspirant non-precipitable when tested by the addition of ammonium hydroxide to establish the pH at 9. We obtain satisfactory results when the proportion of the acid is not more than 2 equivalent weights for each aluminum atom, 1.5 equivalent weights of the acid being particularly satisfactory. With less than 1 equivalent of the acid, the extent of chelation is inadequate. When an alkali metal aluminate is the material treated with hydroxycarboxylic acid and the proportion of acid used exceeds 1.5 equivalents for 1 atom of aluminum, then an alkali metal (Na, K, Li) hydroxide or carbonate is added to establish the necessary pH of 3-9. When the aluminum chlorhydroxy complex is the starting material, then the alkali is added in all cases. The amount of it required to establish the necessary pH varies with the amount of lactic or other acid used.

As the liquid medium for dispersing or dissolving our anionic aluminum antiperspirant, we use ordinarily water or a water solution of a soluble non-tonic, non-irritating organic liquid. Examples of such organic liquids that we use are the alcohols, ethanol, isopropanol, propanol and propylene glycol. The medium chosen must be one in which the aluminum complex is soluble in proportion to give a commercially acceptable antiperspirant effect, as for example, 2.5-7 parts of aluminum calculated as the oxide for 100 parts of the said medium. This corresponds to about 11%-34% of the complex on the dry basis.

Heating is resorted to, particularly when the aluminum is supplied initially in the form of an aluminum chlorhydroxy complex, to accelerate the chelation. The explanation of the acceleration may involve first a decomplexing action on the said complex in contact with the chelating acid. The chelating acid obtains access to the aluminum and the aluminum undergoes chelation so as to withdraw aluminum ion from the system. For this action, heating at a moderate temperature is used. A temperature of 75° C. is a preferred maximum, for lactic acid; and up to 95° C. for gluconic acid. However, if desired, heating to reflux temperature can be achieved.

The heating is continued, as at 60° C.-75° C., as for 2-5 hours, until tests with ionic precipitants for aluminum (ammonia and soluble soap) show no precipitation even on heating with ammonia and the soap, such as sodium stearate, for a half hour or so at 70° C. At lower temperatures of chelation, longer time of contact of the acid with the complex are necessary to obtain the non-precipitability.

In a particularly satisfactory method of effecting this so-called decomplexing and chelation, we heat aluminum chlorhydroxy complex of the kind described with water and lactic acid, for instance, at a temperature of 70°-75° C. until the aluminum in the composition is no longer precipitable by ammonia. This requires about 2 hours in a representative run. Then we add an alkali such as sodium hydroxide in amount to establish the pH at about 8-8.5. Then we heat again at 70° C. for at least about 1 hour, i.e., until the resulting material shows no precipitation (no clouding) on being dissolved in an alcoholic solution of sodium stearate or like alkali metal soap and heated at 70° C. for one-half hour.

The chelated composition made with the heating step gives stable compositions when stirred into hot alcohol solutions of soap and remains stable and non-clouding when the resulting solution is cooled, in the next step according to our invention, and is thus set to a gel.

The proportion of soap used in the alcohol solution with vary somewhat with the nature of the soap and the specific alcohol selected, in accordance with known technique for making gels by dissolving soaps in hot alcohols

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and cooling to cause setting to gel form. Thus there may be used 10-30 parts of a normally solid, alcohol soluble soap, of which sodium stearate is an example, for 100 parts of the alcohol calculated to the anhydrous basis. When the alcohol used is ethanol, either denatured or undenatured, a suitable proportion is about 16-24 parts of the soap for 100 of the ethanol.

Satisfactory soaps that illustrate the class to be used are the sodium salts of stearic, palmitic, and lauric acids.

In respect to antacids, and liquid antiperspirants, and by liquid antiperspirants as used herein is meant both antiperspirants which are used in the form of a liquid and liquid antiperspirants which are subsequently converted into solid antiperspirants, alkali metal aluminum carboxylic acid chelates are provided, alkaline earth metal aluminum carboxylic acid chelates are provided, and also, there are provided the aluminum carboxylic acid chelates of zinc, aluminum, ammonium, and of zirconyl, namely  $(\text{ZrO})^{2+}$ , and mixtures of the foregoing. These chelates are soluble in water and in the stomach fluids, and are characterized by antacid action immediately upon administration.

Normally, the aluminum is chelated in the anionic part of the molecule, except where aluminum-aluminum complexes are comprehended. By "aluminum-aluminum complexes" are meant those complexes in which the aluminum is present in both the cationic and the anionic part of the molecule. When the aluminum is chelated in the anionic part of the molecule it is associated with the hydroxy group of an alpha- or beta- hydroxy aliphatic carboxylic acid. Ordinarily, from one-half to all of the coordination positions of the aluminum atom are taken up by reaction with the acids. Free carboxylic acid groups of the chelate are taken up by neutralization with aluminum hydroxide or aluminate and the resulting salt is water soluble.

The process of the invention, whereby such complexes are prepared, comprises reacting an aluminum compound with a chelating alpha- or beta-hydroxy aliphatic carboxylic acid, and establishing the pH in the finished product by addition of a non-toxic alkaline earth metal hydroxide or basic salt of the aforesaid alkaline earth metals, or by the use of a non-toxic alkali metal hydroxide or basic salt, such as sodium, potassium, lithium hydroxide or carbonate, or the oxide, hydroxide, carbonate or basic carbonate of zinc or aluminum or zirconium, and mixtures thereof, to within the range of a pH of between 4 to about 9. In the case of zirconium, and where aluminum appears in the cationic portion of the molecule, the pH can go as low as about 3.

Aluminum compounds are the most widely used antiperspirants commercially. Many types of aluminum compounds have been used, ranging from relatively water-insoluble compounds, such as aluminum hydroxide, which has a relatively low activity, because of the small amount of aluminum ion provided in aqueous solution, to quite soluble but corrosive aluminum compounds, such as aluminum chloride, aluminum sulfate, and aluminum sulfamate. These compounds have the disadvantage that the high antiperspirant activity obtained due to the very high water solubility and subsequent hydrolysis of the compound is offset by the corrosive action of the acid which remains after the aluminum is taken up by reaction with perspiration acids. Aluminum chlorhydroxy complexes have recently become available, and have proven very successful antiperspirants, because they supply a high concentration of aluminum ion and are not corrosive.

However, all of the aluminum compounds in use today when they supply a sufficiently high concentration of aluminum ions to be effective antiperspirants will not form clear or stable compositions in the presence of soap, because the aluminum reacts with the soap to form insoluble aluminum soaps which precipitate or are incompatible in the composition, thus degenerating into a soft

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non-homogeneous mush. Thus, compositions using soluble aluminum compounds as the antiperspirant have not been successfully formulated in homogenous soap sticks and gels.

5 Aluminum has a coordination number of 4 or 6, usually 6, and will form chelates with various types of organic compounds, such as the alpha- and beta-hydroxy aliphatic organic acids.

In the case of an antacid, the concentration of aluminum ion can be very low. Aluminum hydroxide is an effective antacid, and because aluminum ion will be released from the chelate as fast as it is removed from the stomach fluids by reaction with stomach acids, a fully complexed aluminum chelate is useful as an antacid. However, the aluminum ion concentration is insufficient to provide antiperspirant activity. In fact, even aluminum hydroxide is not regarded by most authorities as being an effective antiperspirant, and aluminum hydroxide supplies a higher concentration of aluminum than a fully complexed aluminum organic acid chelate.

In accordance with the invention, each of the aforementioned compounds, namely the alkali metal aluminum carboxylic acid chelates, the alkaline earth metal aluminum carboxylic acid chelates, and the aforementioned compounds of zinc, zirconium, aluminum-aluminum (namely where the aluminum is present in the cationic portion of the molecule as well as in the anionic portion of the molecule), and ammonium, and mixtures thereof are provided in which aluminum is incompletely complexed, so that as many as 6 and as few as 2 of the 6 coordination positions of the aluminum are taken up by reaction with hydroxy aliphatic acid. Inasmuch as in such complexes the aluminum has free positions available for reaction with acid, the chelate has some of the characteristics of aluminum ion. Hence, the chelate itself is active as an antiperspirant, and the antiperspirant activity is not restricted to aluminum ions supplied by ionization of the chelate complex itself. Such a partially complexed aluminum chelate is also more effective as an antacid than a fully complexed chelate, although both are useful for this purpose, in contrast to use as antiperspirants. Such chelates can be employed in the presence of soap, because neither the chelate nor aluminum ion formed by ionization of the chelate is present in sufficient concentration to form an aluminum soap precipitate. It is, of course, possible that any aluminum soap formed by a direct reaction of the chelate with the soap anion is soluble in water, and this may be an explanation of why the chelate itself, if it reacts with the soap, does not form a precipitate. Thus, the chelates of this invention are effective and non-irritating antiperspirants, and when taken internally are outstandingly effective as antacids, yielding both immediate and prolonged relief from hyperacidity.

In the compounds of this invention, the aluminum is chelated in the anionic part of the molecule, by association with the hydroxy and carboxylate groups of an alpha- or beta-hydroxy aliphatic carboxylic acid. Ordinarily, for antiperspirant use, from 2 to 4 of the coordination positions of the aluminum atom are taken up by reaction with the acid. For antacid use, all 6 of the coordination positions of the aluminum can be taken up, but the partially complexed chelates are more effective, and are preferred. Free carboxylic acid groups of the chelate are taken up by neutralization with aluminum (as hydroxide or aluminate) or alkali metal, and the resulting salt is water-soluble.

The process of the invention, whereby such complexes are prepared, comprises reacting an aluminum compound with a chelating alpha- or beta-hydroxy aliphatic carboxylic acid, and establishing the pH in the finished product by addition of one of the aforesaid metals or ammonium M in the form of its hydroxide, or a basic salt, or ammonium hydroxide, if necessary, as heretofore indicated to within the range from about 3 to about 9. When the compound is to be used in a soap stick type of anti-

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perspirant the pH is generally adjusted to at least 7 whereas when it is to be used in a liquid solution, either as an antacid or as a liquid antiperspirant in spray form or the like, the pH is adjusted to at least 4. If the starting aluminum compound is a strongly basic compound such as an alkali metal aluminate, sufficient alkali metal is generally present in solution so that it may not be necessary to subsequently add additional quantities of a basic alkali metal compound to the mixture to raise the pH thereof. In some cases, it may even be necessary to add additional acid to lower the pH to the desired level.

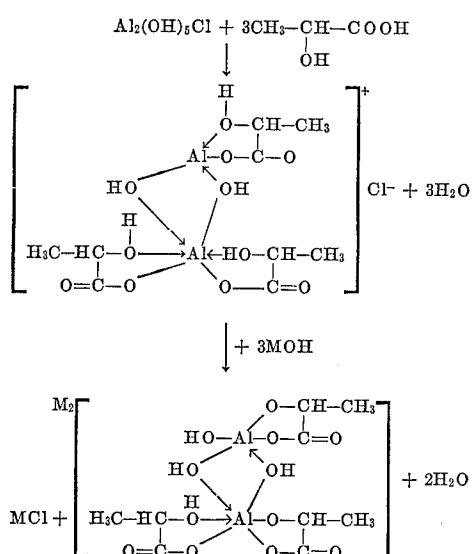
In order to prepare the aluminum chelates of the invention, it is important to react the aluminum compound with the hydroxy carboxylic acid under carefully controlled conditions. As the aluminum compound in preparing a chlorine-free product, an alkali metal or ammonium aluminate can be employed, such as sodium or potassium or ammonium aluminates, or reactive aluminum hydroxide such as in the form of the gel, either dry or wet, or aluminum alcoholates, such as aluminum ethylate, 20 aluminum isopropylate, aluminum sec-butoxide, or aluminum tert-butoxide. Chlorine-containing aluminum chelates are obtained by reaction of the acid with an aluminum chlorhydroxy complex corresponding to the formula:



in which the sum of  $x$  and  $y$  is 6, and  $x$  and  $y$  are each at least 1.

A proportion of acid is employed to establish the best pH level for the finished product, and is adequate to take up at least 3 up to a total of preferably 4 but optionally 6 of the coordinating positions of the aluminum, which total 6. The number of positions taken up by one mole of the hydroxy carboxylic acid will depend upon the available chelating groups in the acid. In the case of lactic acid, one mole of the acid will take up 2 coordination positions, 2 moles will take up 4 of the coordination positions, and 3 moles will take up 6. Thus, in the case of lactic acid, from 1 to 3 moles of the acid per aluminum atom give satisfactory results.

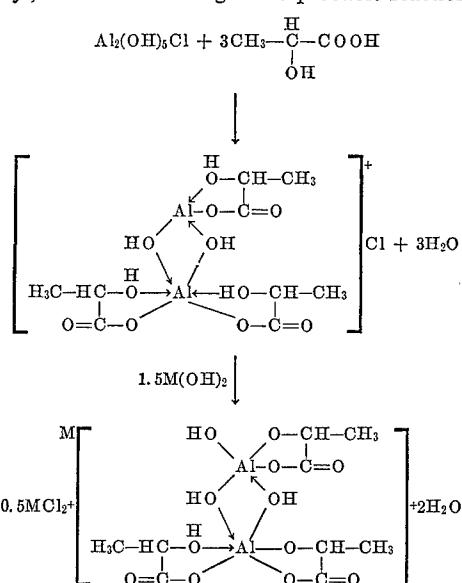
For example, 1.5 moles of lactic acid per aluminum atom give the following probable reaction:



In the foregoing example M is a monovalent cation such as ammonium, lithium, sodium or potassium. Where

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M is divalent, such as zinc, magnesium, calcium, or zirconyl, then the following is the probable reaction:



In the case of citric acid, if all three of the carboxylic acid groups and the hydroxyl group react, one mole of the acid will take up four coordination positions of each aluminum atom. However, all of these chelating groups need not react, and in this event a greater amount of the acid could be used without fully coordinating the aluminum. After all of the acid has been chelated with the aluminum, the pH of the composition is adjusted to within the desired range. Where the chelate is prepared by reacting the acid with aluminum chlorhydroxy complex, the pH of the resulting solution is frequently too low and must be increased to within the range of 3 to 9 by the addition of one of the aforesaid metals or ammonium M in the form of its hydroxide, or a basic salt, or ammonium hydroxide. Where an alkali metal or ammonium aluminate is the starting reactant the pH, if too high, can be adjusted downwardly by the addition of an acid such as a mineral acid or the chelating acid. In either case, the proportion of M in the complex changes accordingly.

The chelating reaction can be carried out in any aqueous or organic solution of the reactants. Ordinarily, water or an aqueous solution of water-miscible organic liquid can be used, such as any of the aliphatic alcohols, 50 ethanol, glycerol and propylene glycol being exemplary. Polyhydric alcohols such as glycerol and propylene glycol can be used also in organic solutions. The medium chosen must be one in which the aluminum chelate is soluble.

It is usually necessary to heat the reaction solution 55 at an elevated temperature within the range from about 45 to about 95° C., to effect the chelation. Elevated temperatures in particular are required, when the aluminum is supplied initially in the form of an aluminum chlorhydroxy complex. The reaction may involve first a de-60 complexing action on the chlorhydroxy complex, in contact with the chelating acid. The chelating acid obtains access to the aluminum, and the aluminum then undergoes chelation, so as to withdraw aluminum ions from the chlorhydroxy complex into the chelating acid complex.

The heating is continued until chelation is complete. From 2 to 5 hours may be required at temperatures of 70 from 60 to 75° C., and correspondingly longer times at lower temperatures. When reaction is complete, no precipitation of aluminum is obtained when a sample of the solution is heated at 70° C. for about a half hour with an ionic precipitant for aluminum, such as ammonia, in an amount to exceed the isoelectric point, i.e., a pH of 6.5 to 7, and a soluble stearate soap in an amount to precipitate aluminum stearate.

For the completion of the chelation, the pH of the complex is adjusted to the desired level. In the case of antacids and antiperspirants, the pH is adjusted to within the range from about 3 to about 9. pH adjustment is normally accomplished by incorporating a sufficient amount of the aforementioned metals or ammonium M in the form of its hydroxide or basic salt, such as the carbonates, as for example, sodium hydroxide or carbonate or potassium hydroxide or carbonate, or ammonium hydroxide. The metal or ammonium M thus forms a salt with the aluminum chelate, and this salt is water-soluble.

These chelates in an appropriate amount make it possible to adjust the pH in the stomach to above 3 but below 5 for at least one hour without at the same time causing alkalnosis. The chelated solution can be formulated into any form of antacid composition. The solution can be used as such as a liquid antacid. It can be gelled by addition of a suitable gelling agent, such as for example, sodium carboxymethyl cellulose, gelatin, sodium alginate, or pectin. It can also be dried by any convenient method, such as by spray or tray drying, to recover a solid material which is water-soluble and which can be either anhydrous or in the form of a hydrate. The soluble material can, if desired, be taken up on a solid non-toxic carrier, such as calcium carbonate or sodium silicate, so as to increase its bulk, but this usually is not required, and may have the undesirable effect of considerably slowing down the rate of solution of the composition in the stomach following administration, thus converting what could have been an immediate antacid effect into a delayed antacid effect. Nonetheless, in some cases a delayed effect may be desired, so that such an excipient is not always disadvantageous.

The complex chelates of the invention are particularly advantageous as antacid compositions because of their immediate antacid effect, due to their water solubility. They are immediately soluble in the stomach fluids, and immediately effective as antacids as a result. They impart a sustained antacid effect for a long period of time, due to the slowly released but adequate concentration of aluminum ion provided from the complex. Hence, the chelate serves as a reservoir supplying additional aluminum ion as fast as the aluminum ion supply is dissipated, and maintains a considerable reserve supply of aluminum over a one and one-half to two hour period or longer.

In these compositions, the anion portion thus effectively acts as an antacid. Furthermore, the basicity of the aluminum chelates is greater than that of ordinary aluminum hydroxide, because up to three additional coordinating positions of the aluminum are taken up in the chelate with basic ions, as compared with water in the case of aluminum hydroxide.

The chelates of the invention make possible the formulation of antacid systems which can be made to have a pH varying over a wide range, due to the possible variations in the proportions of aluminum chelating acids and metal and ammonium cations M. Thus, it is possible to tailor the proportions of these components of the chelates so as to meet any pH need. It is possible, by proper adjustment of the components of the chelates of the invention, to meet specific pH requirements, and accordingly the antacids of the invention are readily formulated in compositions where close regulation of the pH is desired.

Because the antacids of the invention are water-soluble, they show little or no tendency to adsorb other active ingredients present in the antacid composition. In this respect, they are to be contrasted with aluminum hydroxide, which is a very good adsorbent, and has a tendency to adsorb, and accordingly inactivate, other adjuncts of antacid compositions of which it is a component.

The aluminum chelates of the invention in which the aluminum is incompletely complexed also are useful in the formation of antiperspirant compositions of all types,

such as creams, pastes, roll-on solutions or lotions, and sticks. Because the chelate is insufficiently ionized and provided a concentration of aluminum ion less than that required to form aluminum soaps, these chelates can be used in formulations containing soaps or soap fatty acids, and are completely compatible in such solutions at all pHs within the range from 7 to 9. Because the chelate need not be acid but can be made to have a pH on the alkaline side from 7 to about 9, there is a significant absence of corrosiveness or irritation, and there is a lesser problem in the selection of emulsifying agents. Furthermore, the chelates can be used under conditions at which the salting-out effect is not observed. The composition can be formulated so as to be non-destructive to perfuming agents, because of the wide range of pHs within which the chelate is stable.

The aluminum chelates, because of their solubility in water and miscibility with organic solvents, can be used in high concentrations. The recommended concentration range is from 5% to about 40% of the chelate by weight of the composition. The presence of the acid in the chelate indicates a higher concentration of the chelate, because of the lesser weight proportion of the aluminum than in the case, for example, of aluminum hydroxide. However, this higher proportion introduces no problem, because of the solubility of the chelate.

Cream and paste formulations will normally contain, in addition to the chelate and vehicle, an oil or wax, an emulsifying agent, and a pigment or opacifying agent. Lotions will normally be clear, and will contain an appropriate solvent or mixture of solvents plus a buffer to maintain the desired pH. All formulations will contain small amounts of perfume. Both water-in-oil and oil-in-water type emulsion creams can be employed as the base or vehicle for the aluminum chelate. The art is well aware of the types of formulations, which are conventional, and the aluminum chelates of the invention can be used in all such formulations, because of their solubility, and compatibility with other conventional antiperspirant components. A number of various types of formulations are illustrated in the examples.

The aforesaid metal and ammonium aluminum chelates of the invention are particularly advantageous in the formulation of antiperspirant sticks, because of their compatibility with soaps and soaps and soap fatty acids. When preparing antiperspirant sticks, gels are prepared by stirring the chelates prepared by means of this invention, adjusted to a pH of at least 7, into hot alcohol solutions of soap and thereafter cooling. The proportion of soap used in the alcohol solution will vary somewhat with the nature of the soap and the specific alcohol selected, in accordance with known techniques for making gels by dissolving soaps in hot alcohols and cooling to cause setting to gel form. Thus, there may be used from about 10 to about 30 parts of the normally solid alcohol-soluble soap, of which sodium stearate is an example, for 100 parts of the alcohol, calculated on the anhydrous basis. When the alcohol used is ethanol, either denatured or undenatured, a suitable proportion is about 16 to 24 parts of the soap per 100 parts of the ethanol. Satisfactory soaps that illustrate the class of applicable soaps to be used are the sodium salts of stearic, palmitic and lauric acids.

The following examples in the opinion of the inventors illustrate the best embodiments of the aluminum chelates of the invention.

The antacid characteristics of the compounds of the invention are determined by the method of Holbert, Noble, and Grote, Journal of the American Pharmaceutical Association, 36, 149 (1947) and 37, 292 (1948), Journal of the American Pharmaceutical Association, 41, 361 (1952). In this method, a test sample of antacid is added to 150 ml. of pH 1.5 hydrochloric acid containing 2 g. of pepsin N.F. per liter (artificial gastric juice) at

37.5° C. 20 ml. of the artificial gastric juice is withdrawn every 10 minutes, and replaced with an equal volume of fresh gastric juice. The test procedure used in the work reported in the following examples, however, was carried out by continuously introducing fresh artificial gastric juice and removing antacid gastric juice mixture by overflow at the rate of 2 ml. per minute. The antacid effect is determined by measuring the pH of the artificial gastric juice during the test period, which was two hours (120 minutes).

## EXAMPLE 1

71.6 grams of aluminum monochlorohydroxide



(50% aqueous solutions), 82.6 grams of malic acid and 33 grams of deionized water were mixed and heated with agitation for two hours at 60° C. The pH of the resulting solution was 1.1, and was adjusted to 7.0 by reaction with 159.5 grams of 40% potassium hydroxide at 65° C. for 2.5 hours. The resultant product was a clear stable aqueous solution of potassium aluminum chlorhydroxy malate having a potassium content of 13.5%, an aluminum oxide content of 5.46%, a malic acid content of 26.8%, a chlorine content of 1.9%, and a density of 33.0° Baumé at 28° C.

29 ml. of the chelate solution of this invention was diluted to 40 ml., and 10 cc. of the diluted mixture was employed to determine its antacid characteristics by the Holbert, Noble and Grote test method. The results were as follows:

Time, minutes:	pH	35
0	1.5	
0.03	3.0	
0.25	4.7	
0.5	4.7	
1	4.8	40
2	4.8	
3	4.8	
4	4.8	
5	4.8	
6	4.8	
7	4.8	
8	4.8	
9	4.8	
10	4.8	
20	4.6	
30	4.5	50
40	4.2	
50	4.0	
60	3.8	
70	3.6	
80	3.5	55
90	3.3	
100	3.2	
110	3.0	
120	2.9	
130	2.8	60
140	2.7	
150	2.6	
160	2.6	
167	2.5	65

The data shows that this composition was capable of maintaining the pH within the range from 2.5 to 4.8 for 2.8 hours and within the range of 3.0 to 4.8 for 110 minutes. The instantaneous action of the compounds of this invention is particularly noteworthy, since within less than 2 seconds after addition of the antacid composition, the pH was raised from the hyperacid level of 1.5 to a comfortable level of 3.0, and maintained at a pH of at least 3 for 110 minutes, just short of 2 hours.

An oil-in-water type emulsion antiperspirant cream was obtained according to the following formulation:

	Parts by weight
Glycerol monostearate (self emulsifying grade)	18.0
Spermaceti wax	1.7
Stearyl alcohol-ethylene oxide condensate	3.5
Water	6.0
Potassium aluminum chlorhydroxy malate solution	30.8
Perfume, q.s.	

The four ingredients were mixed and heated to 75° C. with agitation, then adding the water and continuing agitation until the temperature had dropped to 37° C., whereupon the perfume and then the active ingredient were blended in. The composition was a smooth cream with excellent antiperspirant activity.

## EXAMPLE 2

56 grams of dried aluminum hydroxide gel, U.S.P. (F-1000), was mixed with 200.8 grams of glucono-delta-lactone and 84 grams of deionized water, and heated at 75° C., with agitation, for 3.5 hours. The pH of the resulting solution was 2.8. Next, 77.3 grams of a 40% aqueous potassium hydroxide solution was added, and heating and agitation were continued to yield a clear solution of potassium aluminum hydroxy gluconate, having a pH of 7.0 and a density of 33° Baumé at 28° C. This solution contained 7.8% potassium, 5.0% aluminum oxide, and 41.1% gluconic acid.

A second batch of this complex was prepared as follows:

28.3 grams of dried aluminum hydroxide gel, U.S.P. (F-1000), was mixed with 100.8 grams of glucono-delta-lactone and 42 grams of deionized water, and heated at 75°, with agitation, for 3.5 hours. The pH of the resulting solution was 2.8. Next, 77.3 grams of a 40% aqueous potassium hydroxide solution was added, and heating and agitation were continued for one-half hour, to yield a clear solution of potassium aluminum hydroxy gluconate, having a pH of 7.0 and a density of 33.7° Baumé at 28° C. This solution contained 7.8% potassium, 5.2% aluminum oxide, and 40.7% gluconic acid.

When tested by the Holbert, Noble and Grote test method, using a 10 cc. dose of mixture containing 50% water and 50% of the chelate solution, the following antacid characteristics were observed:

Time minutes	pH
0	1.5
0.1	3.0
0.25	3.3
0.5	3.4
1	3.5
2	3.6
3	3.7
4	3.7
5	3.7
6	3.7
7	3.7
8	3.7
9	3.7
10	3.7
20	3.7
30	3.6
40	3.5
50	3.4
60	3.3
70	3.2
80	3.1
90	3.0
100	2.9
110	2.8
120	2.8
130	2.6
140	2.5
143	2.5

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These data show that this composition was capable of maintaining the pH above 2.5 for over 2.3 hours.

A satisfactory oil-in-water type of antiperspirant cream was prepared according to the following formulation:

	Parts by weight	5
Glycerol monostearate (self emulsifying grade)	18	
Mineral oil 65/75 cps.	3	
Propylene glycol	3	
Titanium dioxide	1	
Water	25	10
Potassium aluminum hydroxy gluconate	50	

The first five listed ingredients were mixed and heated to 95° C. and then allowed to cool to 35° C. with agitation whereupon the active ingredient was gradually added with agitation to produce a smooth cream with excellent antiperspirant activity.

**EXAMPLE 3**

Sodium aluminum chlorhydroxy lactate was prepared by mixing 122 grams of aluminum chlorhydroxide



50% aqueous solution with 55 grams of deionized water and 77.5 grams of 80% lactic acid and reacting, with agitation, at 60° C. for 2 hours and thereafter adding 33 grams of 50% sodium hydroxide solution to adjust the pH to 6.5. The resultant solution of sodium aluminum chlorhydroxy lactate contained 10.0% aluminum oxide, 21.6% lactic acid, 3.3% sodium and 3.4% chlorine. When tested by the method of Holbert, Noble, and Grote using 5 cc. and 10 cc. doses, the antacid characteristics of the compound were as follows:

Time minutes	pH dose		Time, minutes	pH dose	
	5 cc.	10 cc.		5 cc.	10 cc.
0	1.5	1.5	40	3.8	4.2
0.025	3.0		50	3.8	4.1
0.25	3.8	4.1	60	3.7	4.1
0.5	3.9	4.2	70	3.7	4.0
1	3.9	4.2	80	3.6	4.0
2	3.9	4.2	90	3.5	3.9
3	4.0	4.2	100	3.4	3.8
4	4.0	4.2	110	3.3	3.8
5	4.0	4.2	120	3.2	3.7
6	4.0	4.2	130	3.1	3.6
7	4.0	4.3	140	2.9	3.5
8	4.0	4.3	150	2.8	3.5
9	4.0	4.3	160	2.6	3.4
10	4.0	4.3	170	2.4	3.3
20	4.0	4.3	180	2.3	3.2
30	3.9	4.2	190	2.2	3.1

50

The foregoing data shows the effectiveness of the compound prepared in accordance with this example as an antacid. Within 1.5 seconds after administration of the compound, the pH of the system was raised from the hyperacid level of 1.5 to a comfortable level of 3.0 and the pH was retained above 3.0, without the use of further quantities of the compound, for about 2.3 hours.

**EXAMPLE 4**

Example 3 was repeated using, in place of 33 grams of 50% aqueous sodium hydroxide solution, 37 grams of 50% aqueous sodium hydroxide solution, thereby adjusting the pH to 7.0. The resultant product had aluminum content of 9.9%, a lactic acid content of 21.3%, a sodium content of 3.7% and a chlorine content of 3.4%. The following data was obtained using the method of Holbert, Noble, and Grote, using a 10 cc. dose.

pH  
70  
75

Time, minutes:	pH
0	1.5
1/60	3.0
0.25	4.3
0.5	4.3
1	4.3
2	4.4

Time, minutes:

3	4.4
4	4.4
5	4.4
6	4.4
7	4.4
8	4.4
9	4.4
10	4.4
20	4.4
30	4.3
40	4.2
50	4.2
60	4.1
70	4.0
80	4.0
90	3.9
100	3.8
110	3.7
120	3.6
130	3.6
140	3.5
150	3.4
160	3.3
170	3.2
180	3.1
190	2.9
200	2.8
210	2.6
220	2.5

**20**

Time, minutes:	pH
0	1.5
0.03	3.0
0.25	3.8
0.5	3.9
1	3.9
2	3.9
3	4.0
4	4.0
5	4.0
6	4.0
7	4.0
8	4.0
9	4.0
10	4.0
20	4.0
30	3.9
40	3.8
50	3.8
60	3.7
70	3.6
80	3.5
90	3.4
100	3.3
110	3.2
120	3.1
130	3.0
140	2.8
150	2.7
160	2.5
170	2.4

From the foregoing, it is clear that as little as 5 cc. of the compound prepared in accordance with this example is sufficient to raise the pH from the hyperacid level of 1.5 to an acceptable level of 3.0 in less than 2 seconds and to maintain the pH of this system above 3.0 for over 2 hours.

When a 100 cc. dose of the composition is employed, the pH is raised to above 3.0 in less than 1 second, and is retained above 3.0 for over 3 hours.

**21**  
**EXAMPLE 5**

Sodium aluminum chlorhydroxy lactate was prepared by mixing 2180 grams of a 50% aqueous solution of aluminum chlorhydroxide,  $\text{Al}_2(\text{OH})_5\text{Cl}$ , with 1200 grams of deionized water and 1700 grams of 80% lactic acid, reacting for 2 hours at 70° C. and thereafter adding 940.6 grams of 50% aqueous sodium hydroxide. 581.2 grams of the solution were air dried in a circulating oven at 60° C. for 37 hours to yield 234 grams of water-soluble solid sodium aluminum chlorhydroxy lactate, which was found on analysis to contain 22.1% aluminum oxide, 58.6% lactic acid, 11.7% sodium, and 7.5% chlorine.

A 2.15 grams dose of this solid material, tested by the method of Holbert, Noble, and Grote, exhibited the following antacid characteristics.

Time, minutes:	pH
0	1.5
0.25	3.5
0.5	3.5
1	3.5
2	3.5
3	3.5
4	3.5
5	3.5
6	3.6
7	3.6
8	3.6
9	3.6
10	3.6
20	3.5
30	3.4
40	3.3
50	3.2
60	3.1
70	3.0
80	2.9
90	2.8
100	2.6
110	2.5

An oil-in-water type antiperspirant cream was prepared by mixing the following ingredients in the amounts stated at 70° C.

	Parts by weight
Polyoxylene glycol laurate	5
Glycerol monostearate	5
Butyl stearate	2
Stearic acid	4
Mineral oil (65/75)	8
Cetyl alcohol	3
Cetyl lactate	2

and then adding thereto a mixture of

	Parts by weight
Triethanolamine	1
Propylene glycol	2
Water	28

also maintained at 70° C. There was then added 40 parts of the sodium aluminum chlorhydroxy lactate plus a suitable quantity of perfume.

The product was a smooth cream, with excellent antiperspirant activity. There was no precipitate of aluminum stearate, despite the presence of stearic acid.

**EXAMPLE 6**

Sodium aluminum hydroxy citrate was prepared by mixing an aqueous solution containing 18.2% sodium aluminate with 95 grams of granular citric acid and heating the mixture with agitation at 60° C. for 0.5 hour. Thereafter 44.9 grams of a 50% aqueous sodium hydroxide solution was added, yielding a clear stable solution having a pH of 6.5, an aluminum oxide content of 5.1%, a citric acid content of 27% and a sodium content of 3.9%.

75

**22**

5 and 10 cc. doses showed the following antacid characteristics, using the method of Holbert, Noble, and Grote.

Time, minutes	pH dose		Time, minutes	pH dose	
	5 cc.	10 cc.		5 cc.	10 cc.
0	1.5	1.5	50	3.4	4.9
0.25	4.4	5.9	60	3.2	4.6
0.5	4.5	5.9	70	3.1	4.3
1	4.5	5.8	90	3.0	4.0
2	4.5	5.8	100	2.9	3.7
3	4.5	5.8	110	2.7	3.8
4	4.5	5.8	120	2.6	3.2
5	4.5	5.8	130	2.5	3.1
6	4.5	5.8	140	2.4	3.0
7	4.5	5.8	150		2.9
8	4.5	5.8	160		2.8
9	4.5	5.8	170		2.8
10	4.5	5.8	180		2.6
20	4.1	5.6	190		2.5
30	3.8	5.4	200		2.4
40	3.5	5.1	210		2.3

A 5 cc. test dose was effective in raising the pH from 1.5 to 3.0 in 3 seconds and maintaining the pH above 3.0 for 80 minutes while a 10 cc. dose raised the pH to 3.0 in less than 1 second and maintained it above 3.0 for 3 hours.

**EXAMPLE 7**

Potassium aluminum dihydroxy gluconate was prepared by mixing 70.4 grams of dried aluminum hydroxide gel with 126.5 grams of glucono-delta-lactone and 53 grams of deionized water and heating with agitation at 60° to 70° C. for 5.5 hours. The pH of the resulting solution was 4.5. Thereafter, 50 grams of 40% aqueous potassium hydroxide solution was added, to yield a clear stable solution of potassium aluminum hydroxy gluconate having a pH of 5.75, aluminum oxide content of 7.9% potassium content of 3.0%, gluconic acid content of 30.9%, aluminum to gluconate ratio 0.99 to 1.00 and a density of 27.5° Baumé at 28° C. Excellent antacid characteristics were observed.

A water-in-oil type antiperspirant cream was prepared by mixing the following ingredients at 60° C. and homogenizing.

	Parts by weight
Cholesterol mixture derived from lanolin	24.0
Spermaceti wax	1.5
Water	34.5
Potassium aluminum dihydroxy gluconate	40.0

The resulting smooth cream had excellent antiperspirant activity.

**EXAMPLE 8**

Sodium aluminum chlorhydroxy citrate was prepared by mixing 113.5 grams of aqueous aluminum chlorhydroxide with 98 grams of water and 55 grams of citric acid monohydrate and reacted for 1.5 hours at 60° C. Thereafter, 63.7 grams of the 50% aqueous sodium hydroxide solution was added with agitation. The resultant product was a clear stable aqueous solution having a pH of 8.40, an aluminum oxide content of 10.3%, a citric acid content of 19.7%, a sodium content of 7.05%, and a chlorine content of 3.7%. When tested by the method of Holbert, Noble, and Grote, this solution showed the following antacid characteristics.

Time, minutes	10 cc. dose, pH
0	1.5
0.25	6.3
0.5	6.4
1	6.5
2	6.7
3	6.8
4	7.0
5	7.1
6	7.2
7	7.2

Time, minutes:	10 cc. dose, pH
8	7.3
9	7.4
10	7.5
20	7.5
30	7.4
40	7.1
50	6.8
60	6.3
70	5.8
80	5.5
90	5.2
100	4.8
110	4.3
120	3.8
130	3.4
140	3.2
150	3.1
160	2.9
170	2.9
180	2.8
190	2.7
200	2.7
210	2.6
220	2.6
230	2.5
240	2.4

## EXAMPLE 9

Sodium aluminum chlorhydroxy tartrate was prepared by mixing 89.5 grams of aluminum chlorhydroxide with 49 grams of water and 61.9 grams of tartaric acid and reacting at 65° C. for 2 hours. Thereafter, 57.4 grams of aqueous sodium hydroxide was added, yielding a clear stable aqueous solution of sodium aluminum chlorhydroxy tartrate having a pH of 7.6, an aluminum oxide content of 5.95%, a tartaric acid content of 17.5% and a sodium content of 4.7%. When tested by the method of Holbert, Noble and Grote, using a 10 cc. dose consisting of 2.7 cc. of the solution prepared as above and 1.3 cc. of water, the pH of the system was raised from the hyperacid level of 1.5 to a comfortable level of 3.0 in 1.5 seconds and the pH of the system was maintained above 3.0 for 104 minutes and above 2.5 for 148 minutes.

## EXAMPLE 10

11.3 parts of solid sodium aluminate containing 45% aluminum oxide was dissolved in 100 parts of water and then reacted with 100 parts of an aqueous 13.5% solution of lactic acid. The solution was then heated under reflux for 4 hours, and concentrated by evaporation at a temperature of 70° C. to give a solution of sodium aluminum hydroxy lactate containing 5.6% aluminum oxide. When tested by the method of Holbert, Noble, and Grote, this solution showed good antacid characteristics.

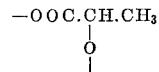
Time, minutes:	8 cc. dose, pH
0	1.5
1/60	3.0
0.25	5.6
0.5	5.6
1	5.6
2	5.6
3	5.6
4	5.6
5	5.6
6	5.6
7	5.6
8	5.6
9	5.6
10	5.6
20	5.4
30	5.2
40	5.1
50	4.9

Time, minutes:	8 cc. dose, pH
60	4.7
70	4.6
80	4.4
90	4.2
100	4.2
110	3.9
120	3.8
130	3.6
140	3.5
150	3.3
160	3.2
170	3.0
180	2.8
190	2.7
200	2.5

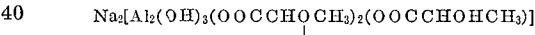
## EXAMPLE 11

118 parts of 85% lactic acid solution was added to 20 155 parts of a 50% aqueous solution of an aluminum chlorhydroxy complex ( $\text{Al}_2(\text{OH})_5\text{Cl}$ , to which were added also 150 parts of water. This complex solution was then adjusted to a pH of 8.25 with 365 parts of 3 N sodium hydroxide and heated at 75° C. until the aluminum therein was not precipitable by ammonia added to pH 9. This required 4 hours. The resulting solution, containing about 4.34% of aluminum calculated as the oxide, was then concentrated to approximately 8.5%  $\text{Al}_2\text{O}_3$  by evaporation at 70° C.

The materials, calculated to molar ratios, correspond to  $\text{Na}_3[\text{Al}_2(\text{OH})_5\text{Cl}(\text{OOCCHOHCH}_3)_3]$ . It is understood that varying proportions of the sodium and chlorine will exist as  $\text{Na}^+$  and  $\text{Cl}^-$  in the solution of the product, and that some at least of the lactate radical will appear as



having two valences, as in the probable formula



A soap stick antiperspirant containing approximately 5%  $\text{Al}_2\text{O}_3$  was made as follows:

45 60 parts of the above concentrated solution (8.5%  $\text{Al}_2\text{O}_3$ ) were stirred into 35 parts of anhydrous denatured alcohol (No. 3A) and 7 parts of commercial sodium stearate in solution in the alcohol. 15 drops of perfume oil (jasmine lavender) were added, the whole being at about 60° C. On cooling, a translucent soap stick (5%  $\text{Al}_2\text{O}_3$ ) in set form resulted, with excellent antiperspirant activity.

50 The chelate solution displaced the following antacid activity, by the Holbert, Noble, and Grote test procedure.

Time, minutes:	7.7 cc. dose pH
0	1.5
0.25	5.1
0.5	5.2
60 1	5.2
2	5.2
3	5.2
4	5.2
65 5	5.2
6	5.2
7	5.2
8	5.2
65 9	5.2
10	5.2
20 20	5.0
30 30	4.7
40 40	4.6
50 50	4.4
60 60	4.2
70 70	4.1
75 80	3.9

Time, minutes:	7.7 cc. dose pH
90	3.8
100	3.6
110	3.5
120	3.3
130	3.2
140	3.0
150	2.8
160	2.7
170	2.5
180	2.4
190	2.3
200	2.2

## EXAMPLE 12

An antiperspirant stick was made as follows: A sodium aluminate solution was first prepared by dissolving 11.3 parts of sodium aluminate ( $45\% \text{ Al}_2\text{O}_3$ ) in 100 parts of water, the water being understood to introduce coordinated hydroxy groups into the molecule of sodium aluminate. The resulting hydroxy-containing sodium aluminate was then reacted with 100 parts of an aqueous solution of lactic acid containing 13.5 parts of lactic acid. There are thus used 1.5 moles of the hydroxycarboxylic acid for 1 gram of aluminum in the aluminate.

The lactate solution so made was heated under reflux for about 4 hours and then concentrated by evaporation at a temperature of  $70^\circ \text{ C}.$ , to give a solution containing approximately 6% of aluminum as  $\text{Al}_2\text{O}_3$ .

Into 50 parts of the hot concentrated solution so made there were then stirred 64 parts of anhydrous denatured alcohol (No. 3A) in which had been dissolved in advance 7 parts of commercial sodium stearate.

The solution, when cooled to ambient temperature, set to a solid cologne stick containing the anionic antiperspirant distributed substantially uniformly throughout.

It is important to limit the concentration of the sodium aluminate solution during the reaction with lactic acid, but not necessarily with all hydroxy carboxylic acids. If the proportion of the sodium aluminum is substantially in excess of 2.5 parts of aluminum calculated as the oxide for 100 of the mixed solutions at the time of reaction with the lactic acid, undesired precipitation occurs. For this reason, the concentration is kept at or below 2.5 parts. After the reaction is effected, then the resulting solution of the sodium aluminum hydroxy lactate may be and suitably is concentrated to an 80% solution concentration or more without causing precipitation.

The product so made does not crystallize or separate on standing. The aluminum is chelated or otherwise contained in a complex to the extent that the aluminum is not precipitated at pH 8.25. The antiperspirant solutions made as described above show special advantages over the aluminum hydroxy type previously used in the making of creams, because of the relatively high pH of the solutions as compared to those of the previous type.

In a modification of this example, a perfume of kind and in amount desired is introduced at some stage before the hot solution is cooled.

Also, a humectant such as propylene glycol, sorbitol, or glycerine in the usual amount may be incorporated in the hot soap solution of either Example 11 or 12.

## EXAMPLE 13

A liquid antiperspirant was made as follows: 63 parts of citric acid USP was dissolved in 340 parts water. To this there was added slowly, with agitation, 38 parts of sodium aluminate (corresponding to about 17 parts  $\text{Al}_2\text{O}_3$ , 1 gram-atom of Al for 1 mole of citric acid) in 330 parts of water. The mixing and resulting reaction gave a solution of pH 8.3 containing the aluminum in the anion.

Aluminum in the solution so made is not precipitable by alkali as shown by the fact that the solution itself is

alkaline. Further, this solution does not cause precipitation when mixed with a hot solution of sodium stearate of the kind described.

The resulting anionic aluminum chelate solution may be used as a spray antiperspirant. For this use, however, the material is concentrated as described above, as to a content of 5% or more of aluminum calculated as  $\text{Al}_2\text{O}_3$ .

## EXAMPLE 14

218 grams of a 50% aqueous solution of aluminum monochlorhydroxide  $\text{Al}_2(\text{OH})_5\text{Cl}$ , 170 grams of 80% aqueous lactic acid, and 120 grams of water were mixed and heated at  $60$  to  $75^\circ \text{ C}.$  for 2 hours. Next, 43.6 grams of magnesium oxide was added, and heating and agitation were continued for 3 hours to yield a clear solution of magnesium aluminum chlorhydroxy lactate, having a pH of 5.3. When diluted with an equal volume of water, the pH was 5.4.

This composition contained 5.8% aluminum oxide and 3.4% magnesium oxide. When tested by the Holbert, Noble, and Grote test method, using 15 cc. of the undiluted product, the antacid characteristics were as follows.

Time, minutes:	pH
0	1.5
1/25	3.0
1/4	3.8
1/2	3.9
1	4.0
2	4.0
3	4.1
4	4.1
5	4.1
10	4.2
20	4.2
30	4.1
40	4.0
50	4.0
60	3.9
70	3.9
80	3.8
90	3.7
100	3.6
110	3.6
120	3.5
130	3.4
140	3.3
150	3.2
160	3.1
170	3.1
180	2.9

The data show that this composition in a 15 cc. dose was capable of maintaining the pH within the range from 3.0 to 4.2 for about 3 hours. The particular effectiveness of this antacid compound is noted from its substantially instantaneous effect. Within 1.5 seconds after addition of the antacid composition, the pH was raised from the hyperacid pH level of 1.5 to a comfortable level of 3.0, and maintained at pH 3 to 4.2 for 3 hours without the addition of further antacid composition. When only 10 cc. of the antacid composition was employed, it took 3 seconds to raise the pH to 3.0 and the pH was maintained at above 3.0 for 130 minutes.

## EXAMPLE 15

62.9 grams of a 50% aqueous chlorhydroxyl solution,  $\text{Al}_2(\text{OH})_5\text{Cl}$ , 102.8 grams of glucono-delta-lactone solution, and 35 grams of water were mixed and heated at  $60$  to  $75^\circ \text{ C}.$  for 2 hours with agitation. There was then added 26 grams of powdered calcium carbonate, and heating and stirring continued for 2.3 hours, yielding a clear solution of calcium aluminum chlorhydroxy gluconate having a pH of 6.4.

The pH data taken in the Holbert, Noble, and Grote test carried out on a 15 cc. sample, are reported below.

Time, minutes:	pH
0	1.5
1/60	3.0
1/4	4.8
1	4.9
2	4.9
3	4.9
4	4.9
5	4.9
10	4.9
20	4.9
30	4.8
40	4.8
50	4.7
60	4.6
70	4.5
80	4.5
90	4.4
100	4.3
110	4.2
120	4.1
130	4.0
140	3.8
150	3.7
160	3.6
170	3.5
180	3.3
190	3.2
200	3.0
210	2.9

The data show that the composition was capable of maintaining the pH within the range from 3.0 to 5.0 for over 3 hours. The unique ability of the compositions of this invention to relieve hyperacidity almost instantaneously is shown by the fact that it took only 1 second for the composition to raise the pH from the hyperacid level of 1.5 to the more comfortable level of 3.0. Furthermore, the composition essentially reached its maximum effectiveness within 15 seconds and retained this effectiveness without diminution for almost 1 hour, thereafter beginning to drop in effectiveness but still being potent enough to keep the pH above 3.0 for an additional 2 hours and 20 minutes. When a smaller dosage was employed (5 cc. instead of 15 cc.), it took 2 seconds for the system to reach a pH of 3.0, and the pH was maintained above 3.0 for about 2 hours.

#### EXAMPLE 16

62.9 grams of chlorhydrol, namely  $\text{Al}_2(\text{OH})_5\text{Cl}$ , was reacted with 102.8 grams of glucono-delta-lactone and 35 grams of water at about 60° C. for about 2 hours. Thereafter, 20 grams of magnesium carbonate was added, and the mixture was reacted for an additional 1.7 hours at about 60° C. to form a clear aqueous solution of magnesium aluminum chlorhydroxygluconate having a pH of 5.5. The pH data taken in the Holbert, Noble, and Grote test carried out on a 15 cc. sample showed that the composition was capable of maintaining the pH within the range from 3.0 to 5.0 for nearly 4 hours.

#### EXAMPLE 17

262 grams of the solution obtained in Example 16 was dried in an air circulating oven maintained at 60° C. for 18.5 hours until a constant weight was achieved, yielding 118 grams of a white, water soluble powder having an aluminum oxide content of 12.6%, a magnesium oxide content of 9.05%, a gluconic acid content of 87% and a chlorine content of 4.3%. The antacid effectiveness of this composition in a 2.3 g. dose was determined, with the following results.

Time, minutes:	pH
0	1.5
1/4	3.2
1/2	3.2

Time, minutes:	pH
1	3.8
2	4.0
3	4.1
4	4.1
5	4.1
6	4.1
7	4.1
8	4.1
9	4.1
10	4.2
20	4.0
30	3.9
40	3.8
50	3.6
60	3.5
70	3.3
80	3.2
90	3.0
100	2.9

Tablets were prepared containing 5 grams each of the antacid powder, 0.5% magnesium stearate, mannitol and dextrose to taste. These tablets were effective antacids, capable of maintaining the pH between 3 and 5 for at least 2 hours, depending on the number of tablets per dose.

#### EXAMPLE 18

106.5 grams of an aqueous chlorhydrol solution was mixed and reacted with 67.6 grams of 80% lactic acid in 48 grams of water for 2 hours. 42.1 grams of magnesium carbonate was then reacted with this mixture for 8 hours at 60° C. The pH was then adjusted with 100 grams of 80% lactic acid to 4.1, yielding a clear, stable aqueous solution of magnesium aluminum chlorhydroxy lactate, having a magnesium oxide content of 2.56%, a lactic acid content of 19.5% and a chlorine content of 1.2%. When administered as an antacid, in a 15 cc. dose, this solution yielded effective results in maintaining the pH of the system between 3 and 5 for at least 2 hours.

#### EXAMPLE 19

28.3 grams of dried aluminum hydroxide gel U.S.P. 50%  $\text{Al}_2\text{O}_3$ , was reacted with 100.8 grams of glucono-delta-lactone in 42 grams of water at 75° C. for 3.5 hours. Thereafter, 25.7 grams of calcium carbonate was reacted for 1 hour at 75° C., yielding a clear, aqueous solution having a pH of 5.4. 4 grams of 40% aqueous potassium hydroxide was added to adjust the pH to 6.5. The resultant product, a potassium calcium aluminum hydroxy gluconate, contained 4.65% calcium oxide, 4.35% aluminum oxide, 34.2% gluconic acid, and 0.3% potassium. The density of the product was 26.8° Baumé at 28° C. The antacid effectiveness of a 10 cc. dose was determined with the following results.

Time, minutes:	pH
0	1.5
1/4	4.0
1/2	4.0
1	4.0
2	4.0
3	4.0
4	4.1
5	4.0
6	4.0
7	4.0
8	4.0
9	4.0
10	4.0
20	3.9
30	3.8
40	3.7
50	3.5

Time, minutes:	pH
60	3.4
70	3.2
80	3.0
90	2.8
	5

## EXAMPLE 20

337.4 grams of the solution obtained in Example 15 was air dried at 60° C. in an air circulating oven for 17 hours to a constant weight of 105 grams. The solid material was a white, water-soluble powder having an aluminum oxide  $\text{Al}_2\text{O}_3$  content of 14.1%, a calcium oxide content of 13.9% and a chlorine content of 4.8%. This powder composition was an effective antacid, capable in a 1.8 g. dose of maintaining the pH of artificial gastric juice between 3 and 5 for at least two hours, as shown by the following data.

Time, minutes::	pH
0	1.5
1/4	3.5
1/2	3.5
1	3.6
2	3.7
3	3.7
4	3.7
5	3.7
6	3.7
7	3.7
8	3.7
9	3.7
10	3.7
20	3.5
30	3.5
40	3.3
50	3.2
60	3.0
70	2.9

## EXAMPLE 21

28.3 grams of aluminum hydroxide dried gel U.S.P. 50%  $\text{Al}_2\text{O}_3$ , was reacted with 100.8 grams of glucono-delta-lactone and 42 g. of water for 3.5 hours at 75° C. To the resulting aluminum hydroxy gluconate (8.2%  $\text{Al}_2\text{O}_3$ ) (100 grams) was added 23.5 grams of magnesium carbonate which was reacted with the solution at 60° C. for 1.5 hours, obtaining a clear, stable solution whose pH was 5.85. 8.5 grams of 40% aqueous potassium hydroxide solution was then added, adjusting the pH to 6.5, and obtaining a clear, stable, aqueous solution of potassium magnesium aluminum hydroxy gluconate containing 0.8% potassium, 4.9%  $\text{Al}_2\text{O}_3$ , 3.3%  $\text{MgO}$ , 38.5% gluconic acid and no chlorine. The density was 28.6° Baumé at 28° C. The antacid effectiveness of this solution was determined, using a 10 cc. dose, with the following results.

Time, minutes:	pH
0	1.5
1/4	4.0
1/2	4.3
1	4.4
2	4.4
3	4.4
4	4.4
5	4.3
6	4.4
7	4.4
8	4.4
9	4.4
10	4.4
20	4.2
30	4.0
40	3.9
50	3.7
60	3.5

Time, minutes:	pH
70	3.4
80	3.2
90	3.0
100	2.8

## EXAMPLE 22

50 grams of aluminum hydroxide dried gel (F-1000) was dissolved in 356.4 grams of glucono-delta-lactone and 300 grams of deionized water at 70° C. in 1 hour. 108 grams of 50% chlorhydrol (aluminum chlorhydroxide  $\text{Al}_2(\text{OH})_5\text{Cl}$ ) was then added, and the solution heated for 2 hours at 60° C. at the conclusion of the chelation to form the aluminum chlorhydroxy gluconate was added 135.5 grams of magnesium carbonate and the solution then heated at 70° C. for 6 hours. A clear, stable, aqueous solution was obtained, magnesium aluminum chlorhydroxy gluconate, having a pH of 7.3, density 28° Baumé at 28° C., and containing 4.6%  $\text{Al}_2\text{O}_3$ , 4.9%  $\text{MgO}$ , 35.1% gluconic acid, and 0.7% chlorine.

This solution was subjected to the Holbert, Noble, and Grote test for antacid effectiveness, using a 10 cc. dose, with the following results.

Time, minutes:	pH
0	1.5
1/4	3.9
1/2	4.0
1	4.0
2	4.1
3	4.1
4	4.1
5	4.1
6	4.1
7	4.1
8	4.1
9	4.1
10	4.1
20	3.9
30	3.7
40	3.6
50	3.4
60	3.2
70	3.0
80	2.8

## EXAMPLE 23

2 grams of calcium lactate was added to 100 grams of a 40% solution of sodium aluminum chlorhydroxy lactate prepared by reacting 218 grams of 50% aluminum chlorhydrol 50% solution (aluminum chlorhydroxide



with 120 grams of deionized water and 170 grams of 80% lactic acid at 60° C. for 2 hours. The solution was heated at 60° C. for 1/2 hour. A clear, stable, aqueous solution resulted, calcium aluminum chlorhydroxy lactate, having a pH of 8.5, 7.95%  $\text{Al}_2\text{O}_3$ , 0.33% calcium oxide, 5.2% sodium, 22.2% lactic acid, aluminum to calcium atomic ratio 18.8:1.

## EXAMPLE 24

369.5 grams of aluminum hydroxide compressed gel U.S.P. (F-2000, 13.8%  $\text{Al}_2\text{O}_3$ ) was reacted with 356.4 grams of glucono-delta-lactone at 60–70° C. for 5 hours. At the conclusion of the chelation to form the aluminum hydroxy gluconate 131 grams of 60%  $\text{Mg}(\text{OH})_2$  paste was then reacted with this solution at 75–80° C. for 2½ hours. A clear, stable, aqueous solution was obtained, magnesium aluminum hydroxy digluconate, having a pH of 7.3, density 30° Baumé at 28° C., and containing 5.6%  $\text{Al}_2\text{O}_3$ , 6.6%  $\text{MgO}$ , and 47.8% gluconic acid.

A 10 cc. dose of this solution was subjected to the Holbert, Noble, and Grote test for antacid effectiveness, with the following results.

## 3,553,316

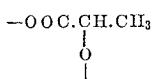
31

Time, minutes:	pH
0	1.5
1/4	4.65
1/2	4.90
1	4.95
2	4.95
3	5.0
4	5.0
5	4.95
6	4.95
7	4.95
8	4.95
9	4.95
10	4.95
20	4.85
30	4.65
40	4.40
50	4.20
60	4.0
70	3.85
80	3.65
90	3.50
100	3.35
120	3.05
140	2.70

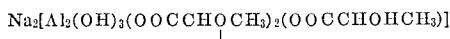
## EXAMPLE 25

118 parts of 85% lactic acid solution were added to 155 parts of a 50% aqueous solution of an aluminum chlorohydroxy complex  $\text{Al}_2(\text{OH})_5\text{Cl}$ , to which were added also 150 parts of water. This complex solution was then adjusted to a pH of 9.25 with 365 parts of 3/N sodium hydroxide and heated at 75° C. until the aluminum therein was not precipitable by ammonia added to pH 9 or by sodium stearate in alcohol solution. This required 4 hours. The resulting solution, containing about 4.34% of aluminum calculated as the oxide, was then concentrated to approximately 8.5%  $\text{Al}_2\text{O}_3$  by evaporation at 70° C.

The materials, calculated to molar ratios, correspond to  $\text{Na}_2[\text{Al}_2(\text{OH})_5\text{Cl}(\text{OOC}-\text{CHOH}-\text{CH}_3)_3]$ . It is understood that varying proportions of the sodium and chlorine will exist as  $\text{Na}^+$  and  $\text{Cl}^-$  in the solution of the product and that some at least of the lactate radical will appear as



formula



A soap stick antiperspirant containing approximately 5%  $\text{Al}_2\text{O}_3$  was made as follows:

60 parts of the above concentrated solution (8.5%  $\text{Al}_2\text{O}_3$ ) were stirred into 35 parts of anhydrous denatured alcohol (No. 3A) and 7 parts of commercial sodium stearate in solution in the alcohol. 15 drops of perfume oil (jasmine lavender) were added, the whole being at about 60° C. On cooling, a translucent soap stick (5%  $\text{Al}_2\text{O}_3$ ) in set form resulted.

## EXAMPLE 26

An antiperspirant stick was made as follows: A sodium aluminate solution was first prepared by dissolving 11.3 parts of sodium aluminate (45%  $\text{Al}_2\text{O}_3$ ) in 100 parts of water, the water being understood to introduce coordinated hydroxy groups into the molecule of sodium aluminate. The resulting hydroxy-containing sodium aluminate was then reacted with 100 parts of an aqueous solution of lactic acid containing 13.5 parts of lactic acid. There are

32

thus used 1.5 equivalents, here also 1.5 moles, of the hydroxycarboxylic acid for 1 atom of aluminum in the aluminate.

The lactate solution so made was heated under reflux for about 4 hours and then concentrated by evaporation at a temperature of 70° C., to give a solution containing approximately 6% of aluminum as  $\text{Al}_2\text{O}_3$ .

Into 50 parts of the hot concentrated solution so made there were then stirred 64 parts of anhydrous denatured alcohol (No. 3A) in which had been dissolved in advance 7 parts of commercial sodium stearate.

The solution, when cooled to ambient temperature, set to a solid cologne stick containing the anionic antiperspirant distributed substantially uniformly therethroughout.

It is important to limit the concentration of the sodium aluminate solution during the reaction with the lactic acid, not necessarily all hydroxy carboxylic acids. If the proportion of the sodium aluminate is substantially in excess of 2.5 parts of aluminum calculated as the oxide for 100 of the mixed solutions at the time of reaction with the lactic acid, undesired precipitation occurs. For this reason, we keep the concentration at or below 2.5 parts. Thus, we avoid the precipitation. After the reaction is effected, then the resulting solution of the sodium aluminum hydroxy lactate may be and suitably is concentrated to as little as 40% or so of its original solution weight without causing precipitation.

The product so made does not crystallize or separate on standing. The aluminum is chelated or otherwise contained in a complex to the extent that the aluminum is not precipitable by ammonia added in amount to establish a pH as high as or somewhat higher. The antiperspirant solutions made as described above show special advantages over the aluminum hydroxy type previously used in the making of creams, because of the relatively high pH of the solutions as compared to those of the previous type.

In a modification of this example, perfume agent of kind and in amount desired is introduced at some stage before the hot solution is cooled.

Also, an humectant such as propylene glycol, sorbitol, or glycerin in usual amount may be incorporated in the hot soap solution of either Example 25 or 26.

## EXAMPLE 27

A liquid antiperspirant was made as follows: 63 parts of citric acid U.S.P. was dissolved in 340 parts water. To this there was added slowly, with agitation, 38 parts of sodium aluminate (corresponding to about 17 parts  $\text{Al}_2\text{O}_3$  or 9 Al, i.e., 1 equivalent of Al for 1 mole of citric acid) in 330 parts of water. The mixing and resulting reaction gave a solution of pH 8.3 containing the aluminum in the anion.

55 Aluminum in the solution so made is not precipitable by alkali as shown by the fact that the solution itself is alkaline. Further, this solution does not cause precipitation when mixed with a hot alcoholic solution of sodium stearate of kind described.

60 The resulting anionic aluminum solution may be used as a spray antiperspirant. For this use, however, the material is concentrated as described above, as to a content of 5% or more of aluminum calculated as  $\text{Al}_2\text{O}_3$ .

## EXAMPLE 28

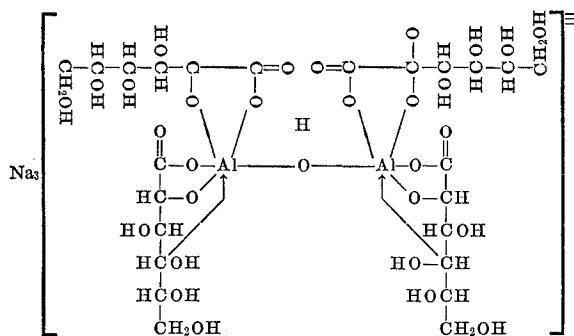
65 Sodium bisgluconatoaluminate III was prepared as follows:

41.5 grams of a 50 weight percent solution of aluminum chlorohydroxide complex containing about 42%



was reacted with 196 grams of a 40% solution of gluconic acid. To this resulting solution there were added 145 milliliters of 3 normal sodium hydroxide after which the pH rose to 8.1. A clear solution resulted.

The reaction product may be shown as a mixture of  $\text{Na}_3[\text{Al}_2(\text{OH})(\text{C}_6\text{H}_{10}\text{O}_7)_4]$  and  $\text{NaCl}$  and may be depicted as:



The gluconate ligands are shown in both the bidentate and tridentate forms. It is not known with certainty which form predominates or whether the bidentate form is actually present to any appreciable degree. Where tridentation is postulated exclusively, then the system may be considered a mixture of the mono and di-sodium aluminum gluconate complexes, or the coordination number of aluminum would have to be assumed to be greater than six.

Alternatively, in the postulation of exclusive tridentation for the gluconate ligands, the bridging hydroxide or "ol" group may be considered to be displaced by gluconate with its subsequent neutralization by an alcoholic hydrogen of the gluconate ligand.

The preparation of potassium bisgluconatoaluminate III is as follows:

#### EXAMPLE 29

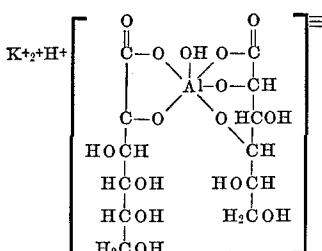
56 grams of dried aluminum hydroxide gel (U.S.P. XV, 75%  $\text{Al}(\text{OH})_3$ ) were reacted with a solution of 200.8 grams of gluconodelta lactone, and 84 grams of water at 75° C. for 3.5 hours with stirring. A clear solution resulted having a pH of 2.8.

145 grams of a 40% weight percent solution of potassium hydroxide was added to the above solution to yield a clear light yellow solution. The pH was found to be 7.0. By calculation, the ratio of K to Al to gluconic acid was found to be 2 to 1 to 2.1.

Reactions:

- $\text{C}_6\text{H}_{10}\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_7$
- $\text{Al}(\text{OH})_3 + 2\text{C}_6\text{H}_{12}\text{O}_7 \rightarrow \text{Al}(\text{OH})(\text{C}_6\text{H}_{11}\text{O}_7)_2 + 2\text{H}_2\text{O}$
- $2\text{KOH} + \text{Al}(\text{OH})(\text{C}_6\text{H}_{11}\text{O}_7)_2 \rightarrow \text{K}_2\text{H}[\text{Al}(\text{OH})(\text{C}_6\text{H}_{10}\text{O}_7)(\text{C}_6\text{H}_9\text{O}_7)] + 2\text{H}_2\text{O}$

The reaction product, potassium hydroxy gluconate may be depicted as:



It is likewise conceivable that the uncoordinated delta hydroxyl group can displace the hydroxide group bonded to aluminum, thereby resulting in 2 similar tridentate gluconate species attached to aluminum, while retaining aluminum's coordination number of 6.

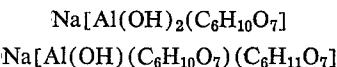
Sodium gluconatodihydroxoaluminate III was prepared as follows:

#### EXAMPLE 30

41.5 grams of a 50 weight percent solution of aluminum chlorhydroxide containing (42%  $\text{Al}_2\text{OH}_5\text{Cl}$ ) were reacted with 147 grams of 40% gluconic acid.

The resulting clear solution was then further reacted with 120 milliliters of 3 normal sodium hydroxide to yield a clear solution of pH=8.33.

The reaction products may be shown as a mixture of



and  $\text{NaCl}$ .

Trisodium bistartratohydroxodialuminate III may be prepared as follows:

#### EXAMPLE 31

150 grams of tartaric acid (U.S.P. grade) were dissolved in 1000 milliliters of water and reacted with 113 grams of sodium aluminate (45%  $\text{Al}_2\text{O}_3$ ) made up to 965 milliliters total volume with water. A viscous solution, somewhat cloudy in appearance resulted which was further diluted with 250 milliliters of water. This system was allowed to agitate at 19° C. to 37° C. for about 7 hours.

The reaction product was essentially trisodium bistartratohydroxodialuminate III.

The preparation of sodium aluminum lactate is as follows:

#### EXAMPLE 32

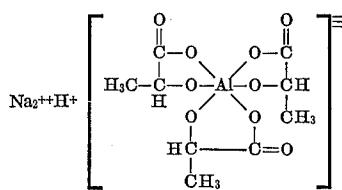
265 grams of U.S.P. aluminum hydroxide gel containing 12.8%  $\text{Al}_2\text{O}_3$  was reacted with and dissolved in 225 grams of 80 weight percent lactic acid. The solution cleared after about one-half hour at 35°–95° C.

To 100 grams of the above aluminum lactate solution were added 21.5 grams of a 50 weight percent sodium hydroxide solution. This resulted in a clear solution of sodium aluminum lactate whose pH was found to be 8.5.

Reactions:

- $2\text{Al}(\text{OH})_3 + 6\text{CH}_3\text{CHOHCOOH} \rightarrow 2\text{Al}(\text{OOCCHOHCH}_3)_3 + 3\text{H}_2\text{O}$
- $2\text{NaOH} + \text{Al}(\text{OOCCHOHCH}_3)_3 \rightarrow \text{Na}_2\text{H}[\text{Al}(\text{OOCCHOHCH}_3)_3] + 2\text{H}_2\text{O}$

The reaction product may be depicted as:



50 sodium aluminum lactate.

The preparation of sodium aluminum citrate was as follows:

#### EXAMPLE 33

A one-third basic aluminum citrate was prepared by reacting 1000 grams of U.S.P. aluminum hydroxide gel (10.2%  $\text{Al}_2\text{O}_3$ ) with 279 grams of citric acid monohydrate (Merck). One liter of water was added to achieve fluidity and heat and agitation applied. The system was heated from 42° C. to 70° C. for about 15 minutes. 85 grams of 50 weight percent sodium hydroxide solution were then added and a clear solution resulted, the pH of which was 5.8.

Reactions:

- $3\text{Al}(\text{OH})_3 + 2\text{C}_6\text{H}_8\text{O}_7 \rightarrow \text{Al}_3(\text{OH})_3(\text{C}_6\text{H}_5\text{O}_7)_2 + 3\text{H}_2\text{O}$
- $\text{NaOH} + \text{Al}_3(\text{OH})_3(\text{C}_6\text{H}_5\text{O}_7)_2 \rightarrow \text{NaH}[\text{Al}_3(\text{OH})_3(\text{C}_6\text{H}_4\text{O}_7)_2] + \text{H}_2\text{O}$

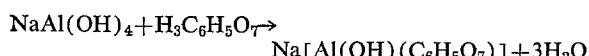
#### EXAMPLE 34

Another method for making sodium aluminum citrate is as follows:

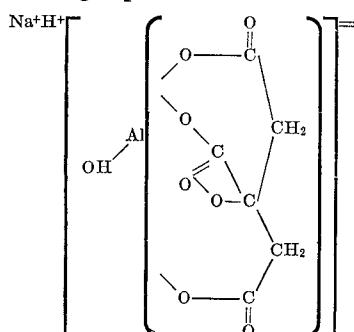
63 grams of citric acid monohydrate were dissolved in 240 grams of water and reacted with 33.9 grams of sodium aluminate (45%  $\text{Al}_2\text{O}_3$ ) which was previously dissolved

## 35

in 300 grams of water. A clear solution resulted, the pH of which was found to be 3.0.



The reaction product may be depicted as follows, with the hydroxy hydrogen being shown outside the brackets although it may also be shown as the un-ionized hydroxy or alcoholic group:

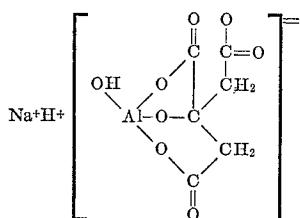


It is conceivable that the hydroxy hydrogen may neutralize the hydroxy group bonded to aluminum in which case a molecule of water would result and the only cation outside the bracket would be sodium with the citrate group being the only ligand attached to aluminum as  $\text{Na}[\text{Al}(\text{C}_6\text{H}_5\text{O}_7)]$ .

Alternatively, since the depiction of 5 and 6 membered chelate rings are theoretically preferable to the citation of 7 membered rings (the above structure has both a 6 and a 7 membered ring formed between aluminum and 1 mole of citric acid), the probable structure may be shown in which one carboxyl group does not participate in ring formation, but instead both 5- and 6-membered rings are formed in which the alcoholic or hydroxy oxygen is common to both, and in which the citrate ligand assumes a tridentate rather than a tetradeinate role, being also a theoretically sound procedure.

The possibility is not contraindicated that the depicted uncoordinated carboxylate group can coordinate to aluminum.

In such a circumstance, two 6-membered rings and one 5-membered ring would then result, all chelated with aluminum.



The hydroxide bonded to aluminum may again conceivably be neutralized by the alcoholic hydrogen shown outside the brackets.

Still another method of making sodium aluminum citrate is as follows:

## EXAMPLE 35

To 320 grams of the product of Example 34 above, there were added 22 milliliters of 3 normal sodium hydroxide to yield a clear solution with a pH of 8.0. Such a solution contains 1.5 moles of sodium per gram atom of aluminum and per mole of citric acid. It may thus be considered a mixture of the mono and disodium aluminum citrate complexes.

Zirconyl dialuminum chlorodihydroxytrilactate was prepared as follows:

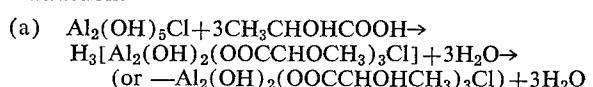
## EXAMPLE 36

218 grams of a 50 weight percent solution of aluminum chlorohydroxide complex,  $\text{Al}_2(\text{OH})_5\text{Cl}$ , were reacted with

## 36

170 grams of 80 weight percent lactic acid and 120 grams of water at  $70^\circ\text{ C}$ . for 2 hours, under reflux, to prevent loss of water to yield dialuminum chlorodihydroxytrilactate.

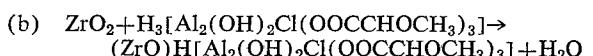
## Reaction:



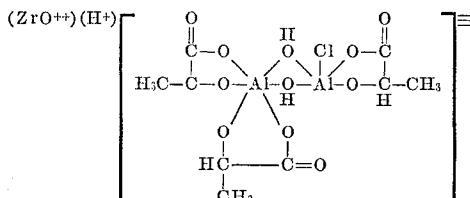
The complex of this reaction is further reacted as follows, in this example, and as shown in Examples 37, 38, 39, and 40.

To 508 grams of the above reaction product, with stirring, there added 61.5 grams of zirconium oxide and maintained to 3.5 hours at  $65^\circ\text{ C}$ . until the zirconium oxide was practically all dissolved. The filtered solution was sparkling clear. After 24 hours, a 1:1 dilution with distilled water of the above zirconyl complex, was found to have a pH of 3.65. The pH of the aluminum complex before the addition of zirconium oxide was 2.70.

## Reaction:



The reaction product may be depicted as:



The reaction product(s) may be shown with the hydroxy hydrogen (of the alpha or beta hydroxy group of the chelating acids), attached to the oxygen as the alcoholic group or alternatively with the hydronium or hydrogen ion outside the brackets as the "partially neutralized" acidic form of the chelate, which taken together with the metal outside the bracket, represent the counterions of the anionic moiety of the chelate complexes.

The preparation of zinc dialuminum chlorodihydroxytrilactate was as follows:

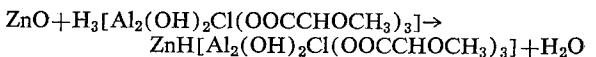
## EXAMPLE 37

Dialuminum chlorodihydroxytrilactate was prepared using the identical procedure set forth in Example 36, part (a).

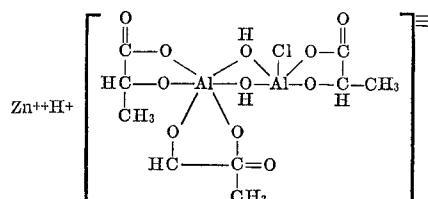
To this material 40.5 grams of zinc oxide ( $\text{ZnO}$ , U.S.P.) were added to the above solution which was at  $60^\circ\text{ C}$ ., in the presence of agitation. After about one hour, the reaction was completed, the zinc oxide having virtually completely dissolved.

The filtered, clear, solution upon 1:1 dilution with distilled water had a pH of 4.38.

## Reaction:



The reaction product may be depicted as:



Aluminum dialuminumchlorodihydroxytrilactate was prepared as follows:

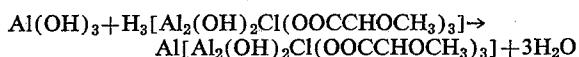
## EXAMPLE 38

Dialuminum chlorodihydroxytrilactate was prepared using the identical procedure set forth in Example 36, part (a).

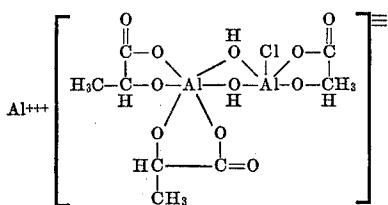
This material was maintained between 50° to 70° C. under agitation, and 50 grams of aluminum hydroxide, U.S.P. XIV powder were added at once. After 2 hours, the aluminum hydroxide was virtually all dissolved.

After filtration, the solution was diluted 1:1 with distilled water and yielded a pH of 3.9.

Reaction:



The reaction product may be depicted as:



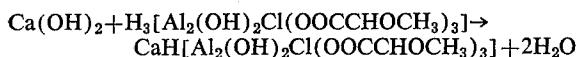
The preparation of calcium dialuminum chlorodihydroxytrilactate was as follows:

#### EXAMPLE 39

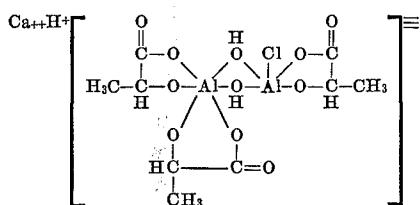
Dialuminum chlorodihydroxytrilactate was prepared using the identical procedure set forth in Example 36, part (a).

To the above solution, in the presence of agitation, there were added 38 grams of calcium hydroxide (97%). After about 1.5 hours at 60°-75° C., the calcium hydroxide virtually completely reacted with an dissolved in the above solution.

Reaction:



The reaction product may be depicted as:



Magnesium dialuminumchlorodihydroxytrilactate was prepared as follows:

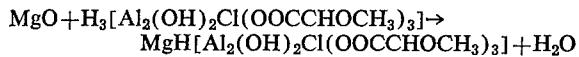
#### EXAMPLE 40

Dialuminum chlorodihydroxytrilactate was prepared using the identical procedure set forth in Example 36, part (a).

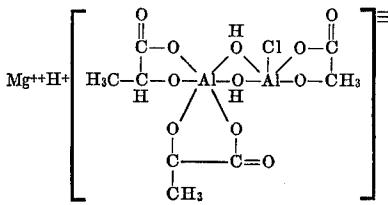
To the above solution, in the presence of agitation, there were added 20.7 grams of magnesium oxide (97% MgO). The reaction was maintained at 50°-75° C. for about one-half hour. It was then allowed to cool for about one hour after which time the magnesium oxide was virtually completely reacted with and dissolved in the aluminum complex.

The pH of a 1:1 dilution of the magnesium complex was found to 5.8.

Reaction:



The reaction product may be depicted as:



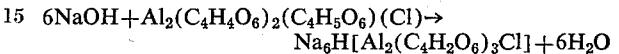
Hexasodium dialuminumchlorotitartrate was prepared as follows:

#### EXAMPLE 41

15 grams of tartaric acid were dissolved in 100 milliliters of water and reacted with 13.5 grams of a 50 weight percent solution of aluminum chlorohydroxide complex, containing 42 weight percent of  $\text{Al}_2(\text{OH})_5\text{Cl}$ .

68 milliliters of a 3 normal sodium hydroxide solution were then reacted with the product of the foregoing to yield a clear solution with a pH of 8.03.

Reactions:



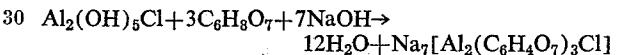
The preparation of heptasodium dialuminumchlorotri-citrate was as follows:

#### EXAMPLE 42

63 grams of citric acid monohydrate were dissolved in 200 milliliters of water and reacted with 41.5 grams of a 50 weight percent solution of aluminum chlorohydroxide complex (42%  $\text{Al}_2(\text{OH})_5\text{Cl}$ ).

The pH of this solution was elevated from 2.30 to 8.45 by reacting it with 245 milliliters of 3 normal sodium hydroxide to form a clear solution.

Reaction:



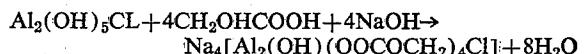
Tetrasodium dialuminum monohydroxychlorotetragly-colate was prepared as follows:

#### EXAMPLE 43

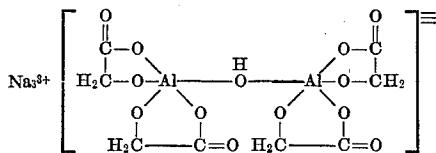
174.4 grams of 50% aluminum chlorohydroxide complex as 42%  $\text{Al}_2(\text{OH})_5\text{Cl}$  were reacted with 128 grams of glycolic acid previously dissolved in 300 grams of water.

620 milliliters of 3 normal sodium hydroxide were then added to the aluminum glycolate solution to yield a clear solution with a pH of 8.30.

Reaction:



The reaction product may also be shown as a mixture of  $\text{Na}_3[\text{Al}_2(\text{OH})(\text{OOCCH}_2)_4]$  and  $\text{NaCl}$  and may be depicted as:

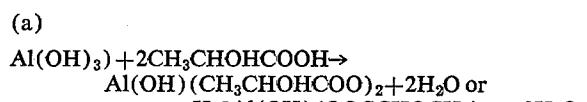


Sodium aluminum lactate was prepared as follows:

#### EXAMPLE 44

79.5 grams of U.S.P. aluminum hydroxide gel (12.8%  $\text{Al}_2\text{O}_3$ ) were dissolved in 45 grams of 80 weight percent lactic acid and 25 grams of water with agitation by the use of heat. The temperature ranged from 48° C. to 90° C. for a period of about 2.5 hours after which a virtually clear solution resulted.

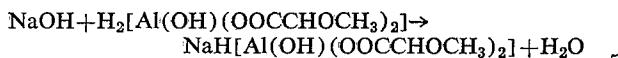
Reaction:



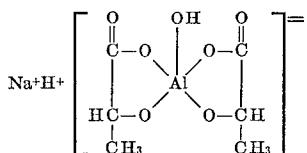
17 grams of a 50 weight percent sodium hydroxide solution were added to the above reaction solution to yield sodium aluminum hydroxy lactate solution with a pH of 7.6.

Reaction:

(b)



The reaction product may be depicted as:



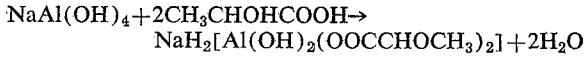
sodium aluminum (hydroxy) lactate.

Another method for preparing sodium aluminum lactate was as follows:

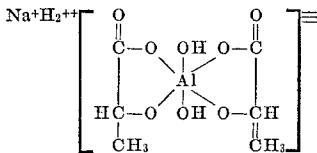
#### EXAMPLE 45

50 grams of water and 36 grams of a 50 weight percent solution of lactic acid were reacted with 11.3 grams of sodium aluminate (45%  $\text{Al}_2\text{O}_3$ ) dissolved in 100 grams of water. The system was heated at 40°–60° C. until it became virtually clear. The pH was found to be 6.5.

Reaction:



The reaction product may be depicted as:

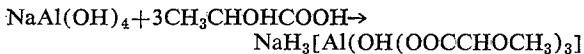


Sodium aluminum lactate was also prepared as follows:

#### EXAMPLE 46

54 grams of water and 54 grams of a 50 weight percent solution of lactic acid were reacted with 11.3 grams of sodium aluminate dissolved in 100 grams of water. The system was heated for about 15 minutes with agitation at 50°–60° C. after which time a clear solution resulted. The pH was found to be 5.5.

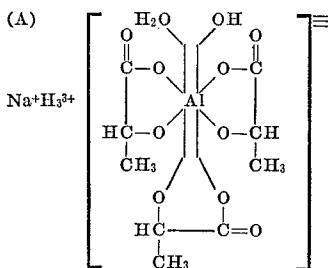
Reaction:



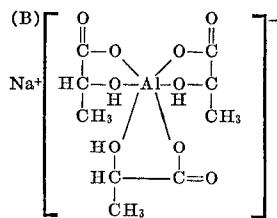
The reaction product may be depicted as either possessing 3 divalent or monovalent moles of lactic acid chelated to aluminum, with a single hydroxy group still bonded to the aluminum. In such a case a molecule of water would be understood to be also attached to aluminum; thus resulting in the assignation of a coordination number of 8 to aluminum, which is a somewhat tenuous assumption in the light of present knowledge.

Alternatively, the reaction product may be depicted in which the hydroxy group is displaced by the chelation of 3 moles of lactic acid. The lactic acid hydroxy hydrogens may be shown outside the brackets with sodium as the counter cations.

Probable reaction product structures:



NOTE: Hydrogen outside bracket may also be shown bonded to original alcoholic oxygen.



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NOTE: Hydroxy or alcoholic hydrogen may also be shown outside the brackets with sodium as in Formula (A).

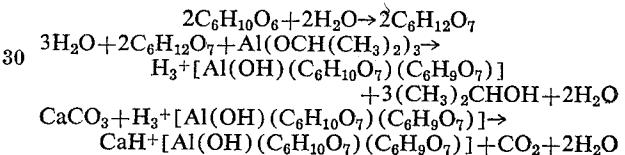
#### EXAMPLE 47

15 Calcium aluminum digluconate was prepared as follows:

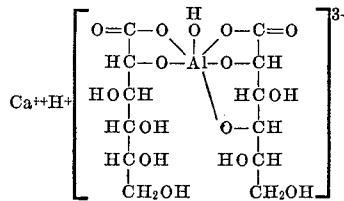
356.2 grams of glucono-delta-lactone was added to 500 milliliters of deionized water and dissolved with the aid of heating to 60° C. 204.2 grams of aluminum isopropoxide was added slowly while refluxing the batch with good agitation. After several hours, a clear solution was obtained.

20 100 grams of precipitated calcium carbonate was added to the above solution under the same conditions. After 25 standing overnight, a slight haze was filtered from the reaction mix yielding a clear stable aqueous solution.

Reaction:



35 The structure of this chelate can be depicted as follows:



45 Examples of chelate complexes prepared in accordance with the present invention include:

- (1)  $(\text{ZrO})\text{H}[\text{Al}_2(\text{OH})_2\text{Cl}(\text{OOCCHOCH}_3)_3]$   
Zirconyl dialuminum chlorodihydroxy trilactate
- (2)  $\text{ZnH}[\text{Al}_2(\text{OH})_2\text{Cl}(\text{OOCCHOCH}_3)_3]$   
Zinc dialuminum chlorodihydroxy trilactate
- (3)  $\text{Al}[\text{Al}_2(\text{OH})_2\text{Cl}(\text{OOCCHOCH}_3)_3]$   
Aluminum dialuminum chlorodihydroxy trilactate
- (4)  $\text{CaH}[\text{Al}_2(\text{OH})_2\text{Cl}(\text{OOCCHOCH}_3)_3]$   
Calcium dialuminum chlorodihydroxy trilactate
- (5)  $\text{MgH}[\text{Al}_2(\text{OH})_2\text{Cl}(\text{OOCCHOCH}_3)_3]$   
Magnesium dialuminum chlorodihydroxy trilactate
- (6)  $\text{NaH}[\text{Al(OH)}(\text{OOCCHOCH}_3)_2]$   
Sodium aluminum monohydroxy dilactate
- (7)  $\text{NaH}_2[\text{Al(OH)}_2(\text{OOCCHOCH}_3)_2]$   
Sodium aluminum dihydroxy dilactate
- (8)  $\text{NaH}_3[\text{Al(OH)}(\text{OOCCHOCH}_3)_3]$   
Sodium aluminum hydroxy trilactate
- (9)  $\text{NaH}_2[\text{Al}(\text{OOCCHOCH}_3)_3]$   
Sodium aluminum trilactate  
(Sodium aluminum lactate)
- (10)  $\text{Na}_6\text{H}[\text{Al}_2(\text{C}_4\text{H}_2\text{O}_6)_3\text{Cl}]$   
Hexasodium dialuminum chlorotritartrate
- (11)  $\text{Na}_7[\text{Al}_2(\text{C}_6\text{H}_4\text{O}_7)_3\text{Cl}]$   
Heptasodium dialuminum chloro tricitrate

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- (12)  $\text{Na}_4[\text{Al}_2(\text{OH})(\text{OOCOCOCH}_2)_4\text{Cl}]$   
Tetrasodium dialuminum monohydroxy tetraglycolate
- (13) Sodium calcium aluminum chlorhydroxy lactate
- (14) Magnesium aluminum chlorhydroxy lactate
- (15) Tetrasodium dialuminum chlorhydroxy monocitrate
- (16)  $\text{Na}_5\text{H}[\text{Al}_3(\text{OH})_3(\text{C}_6\text{H}_{10}\text{O}_7)_6]$   
Sodium aluminum hydroxy gluconate
- (17)  $\text{Ca}_7[\text{Al}_5(\text{OH})_5(\text{C}_6\text{H}_{10}\text{O}_7)_6(\text{C}_6\text{H}_9\text{O}_7)_4]$   
Calcium aluminum hydroxy gluconate
- (18)  $\text{Mg}_6[\text{Al}_5(\text{OH})_5(\text{C}_6\text{H}_{10}\text{O}_7)_8(\text{C}_6\text{H}_9\text{O}_7)_2]$   
Magnesium aluminum hydroxy gluconate
- (19)  $\text{Mg}_3(\text{Ca}_2[\text{Al}_2(\text{OH})_2(\text{C}_6\text{H}_{10}\text{O}_7)_3(\text{C}_6\text{H}_9\text{O}_7)]_2)$   
Magnesium calcium aluminum hydroxy gluconate
- (20)  $\text{K}_5\text{H}[\text{Al}_3(\text{OH})_3(\text{C}_6\text{H}_{10}\text{O}_7)_6]$   
Potassium aluminum hydroxy gluconate
- (21)  $\text{Na}_9\text{H}[\text{Al}_{10}(\text{OH})_{20}(\text{C}_6\text{H}_{10}\text{O}_7)_{10}]$   
Sodium aluminum hydroxy gluconate
- (22)  $\text{K}_9\text{H}[\text{Al}_{10}(\text{OH})_{20}(\text{C}_6\text{H}_{10}\text{O}_7)_{10}]$   
Potassium aluminum hydroxy gluconate
- (23)  $\text{Ca}[\text{Al}(\text{OH})_2(\text{C}_6\text{H}_{10}\text{O}_7)]_2$   
Calcium aluminum dihydroxy gluconate
- (24)  $\text{Mg}[\text{Al}(\text{OH})_2(\text{C}_6\text{H}_{10}\text{O}_7)]_2$   
Magnesium aluminum dihydroxy gluconate
- (25)  $\text{MgCa}[\text{Al}(\text{OH})_2(\text{C}_6\text{H}_{10}\text{O}_7)]_4$   
Magnesium calcium aluminum dihydroxy gluconate
- (26)  $\text{Mg}_2[\text{Al}(\text{C}_6\text{H}_{10}\text{O}_7)_2(\text{C}_6\text{H}_9\text{O}_7)]$   
Magnesium aluminum trigluconate
- (27)  $\text{MgCa}[\text{Al}(\text{C}_6\text{H}_{10}\text{O}_7)_2(\text{C}_6\text{H}_9\text{O}_7)]$   
Magnesium calcium aluminum trigluconate
- (28)  $\text{Na}_3[\text{Al}(\text{C}_6\text{H}_{10}\text{O}_7)_3]$   
Sodium aluminum trigluconate  
(Sodium aluminum gluconate)
- (29)  $\text{K}_3[\text{Al}(\text{C}_6\text{H}_{10}\text{O}_7)_3]$   
Potassium aluminum trigluconate  
(Potassium aluminum gluconate)
- (30)  $\text{Na}_3\text{H}_3[\text{Al}_2(\text{C}_6\text{H}_4\text{O}_7)_3]$   
Trisodium dialuminum tricitrate
- (31)  $\text{Ca}_2[\text{Al}_2(\text{OH})_3(\text{C}_6\text{H}_9\text{O}_7)_2\text{Cl}]$   
Dicalcium dialuminum chlorotrihydroxy digluconate
- (32)  $\text{Mg}_8[\text{Al}_2(\text{OH})(\text{C}_6\text{H}_{10}\text{O}_7)_4\text{Cl}]$   
Octamagnesium dialuminum chlorhydroxy tetragluconate
- (33) Sodium aluminum chlorhydroxy citrylmonogluconate
- (34) Sodium aluminum chlorhydroxy citryldigluconate
- (35) Sodium aluminum hydroxycitrylmonogluconate
- (36)  $\text{K}_3\text{H}_5[\text{Al}_2(\text{C}_4\text{H}_3\text{O}_5)_4\text{Cl}]$   
Tripotassium dialuminum chloro tetramalate
- (37)  $\text{KCaH}[\text{Al}(\text{OH})(\text{C}_6\text{H}_9\text{O}_7)_2]$   
Potassium calcium aluminum hydroxy digluconate
- (38) Potassium magnesium aluminum hydroxy digluconate
- (39)  $\text{Ca}_2[\text{Al}(\text{C}_6\text{H}_{10}\text{O}_7)_2(\text{C}_6\text{H}_9\text{O}_7)]$   
Calcium aluminum trigluconate  
(Calcium aluminum gluconate)

The disclosures of U.S. patent applications Ser. Nos. 668,886; 236,168; and 255,218 are incorporated herein by reference.

It is claimed:

1. A process for the preparation of an anionic antiperspirant comprising the steps of forming a mixture of

- an aqueous solution of a compound selected from the group consisting of aluminum chlorhydroxy complexes containing approximately 1.5-2.5 atoms of aluminum for 1 atom of chlorine and alkali metal aluminates with a non-toxic, water and alcohol soluble hydroxycarboxylic acid selected from the group consisting of lactic, citric, tartaric, and mixtures thereof in the proportion of 1-2 equivalent weights of the acid for 1 atom of aluminum, adding alkali in an amount required to establish a pH of 4-9, and maintaining contact between said compound and said acid at said pH to form an aluminum-containing product which at a pH of 8-9 becomes soluble in a test solution of sodium stearate in alcohol and the aluminum is non-precipitable therein on heating to 70° C.
2. A process according to claim 1 in which the said compound is an aluminum chlorhydroxy complex containing 1.5-2.5 atoms of aluminum to 1 atom of chlorine, the aqueous chlorhydroxy complex and the acid are heated together at a temperature not above 75° C. until the aluminum content no longer is precipitable on mixing with a test solution of ammonium hydroxide, the alkali is selected from the group consisting of alkali metal hydroxides and carbonates and is added to the heated mixture, and heating at the said pH and temperature is continued until the aluminum becomes non-precipitable at 70° C. and at a pH of 8-9 in a test solution of sodium stearate in alcohol.
3. A process according to claim 1 in which said acid is lactic acid.
4. A composition of matter comprising the anionic reaction product of an aluminum compound selected from the group consisting of aluminum chlorhydroxy complexes containing 1.5-2.5 atoms of aluminum for 1 atom of chlorine and alkali metal aluminates with a non-toxic, water and alcohol soluble hydroxycarboxylic acid selected from the group consisting of lactic, citric, tartaric and mixtures thereof in the proportion of 1-2 equivalent weights of the acid for 1 atom of aluminum in the said compound and then an alkali in an amount required to establish a pH of 4-9, said anionic product being soluble in alcohol and in water and the aluminum in the product being non-precipitable on being brought at pH 8-9 into contact and warmed with sodium stearate dissolved in alcohol; and an aqueous solution of a soluble non-toxic non-irritating organic liquid, said anionic product being dissolved therein sufficiently to provide 2.5 to 7 parts of aluminum, calculated as the oxide, to 100 parts of the liquid.
5. The composition of claim 4 in which the said reaction product is of an aluminum chlorhydroxy complex containing 1.5-2.5 atoms of aluminum for 1 of chlorine and the said anionic composition contains 1-1.6 atoms of sodium for 1 atom of aluminum.
6. The composition of claim 4 in which the acid is lactic acid.
7. The composition of claim 4 in which said liquid is selected from the group consisting of ethanol, isopropanol, propanol and propylene glycol.
8. An antiperspirant stick comprising the reaction product of (a) an aluminum compound selected from the group consisting of alkali metal aluminates and aluminum chlorhydroxy complexes containing 1.5 to 2.5 atoms of aluminum for 1 atom of chlorine with (b) a non-toxic, water and alcohol soluble hydroxycarboxylic acid selected from the group consisting of lactic, citric, tartaric and mixtures thereof in the proportion of 1-2 equivalent weights of (b) for each 1 atom of aluminum in (a), and (c) an amount of alkali sufficient to establish a pH of 4-9 and an alcohol solution of an alkali metal soap, the antiperspirant being dissolved in the said solution, the solution being set in gel form, and the pH of the stick being approximately 7.5-9.
9. An antiperspirant stick in accordance with claim 8 wherein the reaction product is formed from the alkali metal aluminate.

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10. The antiperspirant stick of claim 8 in which the proportion of alcohol in the stick is about 30-40 parts for 100 of the stick.

11. The antiperspirant stick of claim 8 in which the concentration of the said antiperspirant is 4-5.5 parts calculated as  $\text{Al}_2\text{O}_3$  for 100 of the stick.

12. A stable antiperspirant stick having a pH of at least 7, said stick having a base comprising sodium stearate, water and a lower alkyl monohydric alcohol, and said stick having therein, as an antiperspirant, a lactate complex of an aluminum-containing chemical.

13. A process for the preparation of an anionic antiperspirant in stick form comprising the steps of: forming a mixture of an aqueous solution of a compound selected from the group consisting of alkali metal aluminates and aluminum chlorhydroxy complexes containing approximately 1.5-2.5 atoms of aluminum for 1 atom of chlorine with a non-toxic, water and alcohol soluble hydroxy carboxylic acid selected from the group consisting of lactic, citric, tartaric and mixtures thereof in the proportion of 1-2 equivalent weights of the acid for 1

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atom of aluminum; adding alkali in an amount sufficient to establish a pH of 4-9; maintaining contact between said compound and said acid at said pH to form an aluminum-containing product which at a pH of 8-9 becomes soluble in a test solution of sodium stearate in alcohol and the 5 aluminum is non-precipitable therein on heating to 70° C.; dissolving said aluminum-containing product in a warm alcoholic solution of sodium stearate; and cooling the resulting solution to the temperature of setting of the solution to a gel.

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ALBERT T. MEYERS, Primary Examiner

VERA C. CLARKE, Assistant Examiner

U.S. Cl. X.R.

20 260—429.3, 429.9, 448; 424—66, 67, 289, 311, 313