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DETERGENT COMPOSITIONS

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No Drawing. Continuation-in-part of application Ser. No. 879,627, Nov. 24, 1969, which is a continuation-in-part of application Ser. No. 731,700, May 24, 1968. This application Oct. 12, 1970, Ser. No. 80,166
Int. Cl. C11d 3/20, 7/26
U.S. Cl. 252—89 5 Claims

ABSTRACT OF THE DISCLOSURE

There are disclosed herein detergent compositions containing a water-soluble organic detergent compound and as a builder therefor the normal alkali metal, ammonium or alkanol amine salts of carboxymethyloxysuccinic acid.

This application is a continuation-in-part of application Ser. No. 879,627, filed Nov. 24, 1969, and issued as U.S. Pat. No. 3,635,830, which in turn is a continuation-in-part of application Ser. No. 731,700, filed May 24, 1968, and now abandoned.

The present invention relates to detergent compositions containing a novel builder therefor.

BACKGROUND

Eutrophication is the process of excessive fertilization of aquatic plants through enrichment of waters with nutrients, such as carbon, nitrogen, phosphorus, potassium, iron, trace metals and vitamins. Factors in the eutrophication of lakes, streams and estuaries are natural runoff, agricultural drainage, groundwater, precipitation, sewage and waste effluents.

Although there is no present adequate proof, it has been postulated that the phosphorus-containing builders present in detergent compositions can be a factor in eutrophication. Therefore any substitutes which do not contain phosphorus may decrease to some extent the eutrophication.

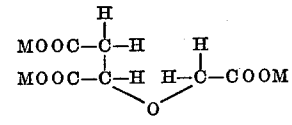
It is, therefore, an object of the present invention to provide detergent compositions with a builder compound which is free of phosphorus.

The compositions of the invention necessarily include both a synthetic builder and a water-soluble organic detergent compound. Such detergent compounds that are useful in the present invention are the anionic (soap and nonsoap), nonionic, zwitterionic and ampholytic compounds. The chemical nature of these detergent compounds is not an essential feature of the present invention. Moreover, such detergent compounds are well known to those skilled in the detergent art and the patent and printed literature are replete with disclosures of such compounds. Typical of such literature are "Surface Active Agents" by Schwartz and Perry and "Surface Active Agents and Detergents" by Schwartz, Perry and Berch, the disclosures of which are incorporated by reference herein.

The phosphorus-free builders for the detergent compositions of the invention are the normal alkali metal, ammonium and lower mono-, di- and trialkanolamine

salts of ether polycarboxylic acids selected from the group consisting of oxydisuccinic acid and carboxymethyloxysuccinic acid. The oxydisuccinic acid is also known as 2,2′-oxydisuccinic acid.

The builder salts of the ether polycarboxylic acids of the present invention can be generally represented as follows:



wherein R is H or —CH_2COOM and M is selected from the group consisting of alkali metal, ammonium and substituted ammonium cations such as morpholinium, alkyl ammonium and mono-, di- and trialkanol ammonium.

Typical of such materials are trisodium carboxymethyloxysuccinate, tripotassium carboxymethyloxysuccinate, trilithium carboxymethyloxysuccinate, triammonium, carboxymethyloxysuccinate, the normal monoethanolamine salt of carboxymethyloxysuccinic acid, the normal diethanolamine salt of carboxymethyloxysuccinic acid, the normal triethanolamine salt of carboxymethyloxysuccinic acid, the normal tetramethylammonium salt of carboxymethyloxysuccinic acid, tri(ethylammonium) carboxymethyloxysuccinate, the normal monoisopropanolamine salt of carboxymethyloxysuccinic acid, the normal diisopropanolamine salt of carboxymethyloxysuccinic acid, monosodium dipotassium carboxymethyloxysuccinate, disodium monopotassium carboxymethyloxysuccinate, the normal morpholine salt of carboxymethyloxysuccinic acid, and the like.

The weight ratio of carboxymethyloxysuccinate builders to detergent compound when used in laundering and hand dishwashing compositions, ranges generally from about 1:20 to about 20:1. When the novel builders are used in mechanical dishwashing compositions, the ratio of builder to detergent compound is from about 10:1 to about 50:1.

The carboxymethyloxysuccinate builders can be used either as the sole builder or where desired can be used in conjunction with other well-known builders, examples of which include oxydisuccinate tetrasodium and tetrapotassium pyrophosphate, pentasodium and pentapotassium tripolyphosphate, trisodium and tripotassium nitrilotriacetate, polyacrylates, starch or cellulose derived polycarboxylates, and the like. Other materials which may be present in the detergent compositions of the invention are those conventionally present therein. Typical examples thereof include the well-known soil suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, fillers, optical brighteners, enzymes, suds boosters, suds depressants, germicides, anti-tarnishing agents, cationic detergents, softeners, chlorine releasing agents, buffers and the like. The balance of the detergent compositions is water.

The detergent compositions of the present invention may be in any of the usual physical forms for such compositions, such as powders, beads, flakes, bars, tablets, noodles, liquids, pastes and the like. The detergent compositions are prepared and utilized in the conventional manner. When using the detergent compositions of the invention to wash clothes, the wash solutions should have a pH from about 7 to about 12, preferably from about 9

to about 11. Therefore, the presence of a buffer in the detergent composition is usually desirable. Examples of such buffers are sodium silicate, carbonate or bicarbonate.

When the pH value of the wash solution is below about 8.6 some of the salts of the carboxymethyloxysuccinic acid will be present in the acid salt form and some in the normal salt form.

An important advantage of the carboxymethyloxysuccinate is its excellent biodegradability characteristics as measured by both standard BOD_5 tests (biochemical oxygen demand for five days) and a modified Soap and Detergent Association's Semicontinuous Activated Sludge Test.

The normal oxydisuccinate builder salts can be prepared in the conventional manner. Thus, the tetrasodium oxydisuccinate may be prepared as follows: An aqueous solution containing 5 grams of oxydisuccinic acid (2,2'-oxydisuccinic acid) in 35 ml. of distilled water is titrated to a pH of 8.6 with a 2 N sodium hydroxide solution. The aqueous solvent is removed under reduced pressure and the residue is tetrasodium oxydisuccinate (tetrasodium 2, 2'-oxydisuccinate). Similarly using carboxymethyloxysuccinic acid and the required amount of sodium hydroxide, the trisodium carboxymethyloxysuccinate can be prepared.

Employing a procedure similar to that given above, the corresponding normal alkali metal, ammonium and substituted ammonium salts of oxydisuccinic acid and carboxymethyloxysuccinic acid can be prepared by using a stoichiometric quantity of the appropriate alkaline reactant. The normal mixed salts of oxydisuccinic acid and carboxymethyloxysuccinic acid can be prepared by neutralizing oxydisuccinic acid or carboxymethyloxysuccinic acid respectively with the requisite proportional amounts of basic compounds containing the desired cations.

A preferred method for preparing the carboxymethyloxysuccinate is to react a mixed alkaline earth metal salt such as the calcium salt of maleic acid and glycolic acid in an aqueous alkaline medium. The pH of the medium should be adjusted with an alkaline earth metal reagent such as calcium hydroxide, strontium hydroxide or barium hydroxide.

It has been found that when the reaction is carried out at a pH range of 10.5 to 12.5 as measured initially at room temperature (about 25° C.) yields of about 80–95% carboxymethyloxysuccinate are obtained in a few hours or less. When the reaction is carried out at a preferred pH of about 11.3 to 12.0 as measured initially at room temperature which corresponds to about 9.9 to 10.3 at 100° C., yields of 90% or better are obtained in less than two hours.

It has also been found that when using a relatively insoluble alkaline earth metal hydroxide such as magnesium hydroxide, the initial pH at room temperature of the reaction mixture even with an excess amount of the hydroxide is only about 8 to 9. However, by heating the reaction mixture at reflux temperatures or heating at superatmospheric pressure, satisfactory yields of the product can be obtained.

The mole ratio of glycolic acid to maleic acid used in the reaction is from about 1:1 to about 2:1 and preferably from 1.05:1 to about 1.2:1. The temperature at which the reaction may be carried out is normal reflux temperature (100–102° C.) or below reflux temperature say, 60° C. However, if the reaction is carried out at temperatures above reflux temperature, 102–200° C., the rate of reaction is increased so that at certain elevated temperatures the reaction may be completed within a matter of minutes.

An interesting intermediate product formed during the reaction of the preferred process is the calcium chelate salt of carboxymethyloxysuccinate corresponding to the following empirical formula: $C_6H_5O_7Ca_{1.5}$. The compound while represented in the anhydrous form is generally obtained in the hydrated form.

This calcium chelate salt corresponds to the calcium salt derived from two moles of the monocalcium chelate of carboxymethyloxysuccinate. The calcium chelate salt and the monocalcium chelate have utility as an animal feed, plant nutrient or any other area requiring calcium. Of course, other alkaline earth metal salts and other polyvalent salts such as zinc, iron, manganese, cobalt and the like could also be formed and used for the same or similar purposes.

While the calcium chelate salt can be isolated directly from the reaction because of its low solubility, the monocalcium chelate, which is highly soluble, must be obtained by either partially decalcifying the calcium chelate salt, e.g., ion exchange resin or, for example, by total decalcification followed by neutralization with one mole of calcium hydroxide and one mole of sodium hydroxide per one mole of carboxymethyloxysuccinic acid. For purposes of convenience, hereinafter the alkaline earth metal or polyvalent metal chelate salts and monoalkaline earth metal or polyvalent chelates of carboxymethyloxysuccinate will be referred to as simply salts of carboxymethyloxysuccinic acid.

While the alkali metal, ammonium and substituted ammonium salts of carboxymethyloxysuccinic acid are very effective builders, they are also effective as boiler scale removers, degreasers, grease cutters and rust and stain removers.

When the oxydisuccinic acid has been prepared in accordance with Example 1 of U.S. Pat. No. 3,128,287 issued to Chas. Pfizer and Company, Inc., it has been found that a mixture of two diastereoisomeric forms of oxydisuccinic acid will be obtained. The less soluble form has been designated as the d,l-racemate. The more soluble diastereoisomer has been designated as the meso form and is found in the aqueous filtrate after decomposition of the calcium salts with sulfuric acid and removal of the less soluble d,l-racemate. Accordingly, mixtures of meso and d,l-oxydisuccinate can be prepared as well as purified d,l-oxydisuccinic acid and a purified meso-oxydisuccinic acid. Thus these materials may be prepared as follows:

Maleic anhydride, 19.6 g. (0.2 mole), is dissolved in 200 ml. of water and heated to 100° C. for five minutes. Calcium hydroxide, 16.0 g. (0.22 mole), is then added and the mixture stirred and refluxed for four days. The insoluble calcium salts are filtered and dried. The dried product, 22 g. is slurried in water and passed through an Amberlite IR–120 cation exchange column to remove the calcium ions. The eluate is then evaporated to dryness to yield 14.5 g. of crude oxydisuccinic acid.

Examples of the detergent compositions of the invention are set forth below as illustrative but not limited to such compositions.

The detergent formulations set forth below are prepared by blending together the recited components and are then tested for detergency or cleansing ability in the Terg-O-Tometer Test wherein the washing conditions are as follows (unless otherwise indicated): 65% Dacron-35% cotton VCD (vacuum cleaner dust) cloth; 120° F.; 180 p.p.m. water (2/1 Ca^{++}/Mg^{++}); 0.15% concentration of the total formulation in the washing solution; pH 9.5. (The pH of the washing solutions given herein was adjusted, where necessary, by the addition of caustic (NaOH) or sulfuric acid thereto.)

The average detergency units (DU) of the formulations is the final reflectance of the washed cloth minus the initial reflectance of the soiled cloth (the average of two runs), the reflectance being measured with a Gardner Automatic Color Difference Meter, Model AC–3.

The following abbreviations have been used in the tables and examples: LAS is an anionic surfactant which is sodium linear secondary alkyl (C_{10}–C_{15}) benzene sulfonate; Neodol 45–11 is a nonionic surfactant which is an adduct of a modified Oxo type C_{14}–C_{15} alcohol with an average of 11 moles of ethylene oxide; C_{14}–C_{16} HAMT is an ampholytic surfactant which is sodium hydroxyalkyl

(C_{14}–C_{16}) N-methyltaurate; (DCH) sulfobetaine is a zwitterionic surfactant which is cocodimethylsulfopropyl betaine; NaODS is tetrasodium oxydisuccinate; STPP is pentasodium tripolyphosphate; TKPP is tetrapotassium pyrophosphate; NTA is trisodium nitrilotriacetate; RU silicate is a sodium silicate having a SiO_2:Na_2O ratio of 2.4:1; DU is detergency units; and bal. is balance.

The effectiveness of the carboxymethyloxysuccinate salts as detergent builders is exemplified in Examples 1–18 and 33–36.

More specifically, Examples 1–10 show the use of trisodium carboxymethyloxysuccinate as a detergent builder with various surfactants. Example 11 describes the use of trisodium carboxymethyloxysuccinate in a machine dishwashing composition. Examples 12–14 illustrate the enhancement of the detergent building properties of trisodium carboxymethyloxysuccinate in the presence of added sodium sulfate. Examples 33–36 show the enhancement of detergent building properties of carboxymethyloxysuccinate by use of higher levels of surfactant.

In all cases except for Example 11 the detergency tests were carried out as set forth in examples above and as modified in the description of the washing conditions stated at the beginning of the examples. In the case of Example 11, the detergency properties were established by washing artificially soiled glasses and dishes in a standard home dishwashing machine and comparing the results with those obtained with a standard sodium tripolyphosphate-built formulation. The artificial soil is a mixture of milk, vegetable residues, lipstick, gravy, starch, eggs and lard.

Examples 15–32 show the preferred method for the preparation of carboxymethyloxysuccinic acid and the salts thereof.

EXAMPLES 12–14

DETERGENCY BUILDING PROPERTIES OF TRISODIUM CARBOXYMETHYLOXYSUCCINATE WITH SODIUM SULFATE

[Washing conditions: Terg-O-Tometer; Dacron/cotton VCD cloth; 120° F. 180 p.p.m. (2:1Ca^{++}/Mg^{++}) water; 0.1% formulation concentration; pH=10.0]

Components	Formulation for Example— 12	13	14
LAS, percent	18	18	18
Trisodium carboxymethyloxysuccinate, percent	40	40	40
STPP, percent			23
Sodium sulfate, percent	23		10
RU-silicate solids, percent	10	10	Balance
Water	Balance	Balance	22.8
Detergency (DU's)	22.7	21.9	96
Percent efficiency (12 vs. 14 and 13 vs. 14)	100	96	

EXAMPLES 15–16

Preferred preparation of trisodium carboxymethyloxysuccinate

Maleic anhydride (0.2 mole; 19.6 g.) is dissolved in water (100 ml.) at room temperature and stirred for 10–15 minutes to convert it to the acid. Glycolic acid (0.24 mole; 18.3 g.) is then added and dissolved with stirring. Calcium hydroxide, (ca 0.36 mole; 27 g.), sufficient to attain a pH of 11.4 as measured initially at 25° C. is next added while stirring the reaction mixture vigorously. The mixture is heated to reflux and maintained at reflux for two hours while stirring vigorously. After cooling to 60° C., finely ground sodium carbonate (0.4 mole; 42.4 g.) is added and stirring continued for fifteen minutes at 60° C. The mixture is then cooled to room temperature and the suspended $CaCO_3$ filtered off and washed with water. The filtrate (including the washings) contains the product, trisodium carboxymethyloxysuccinate, in yields of about 95% as determined by NMR analysis.

The NMR analysis, which can be run before or after treatment with the sodium carbonate, involves taking a 25 ml. sample of the reaction mixture and treating it with a cation exchange resin. After filtering and washing the resin with water, the combined filtrate and washings are evaporated to a residue in vacuo. An NMR analysis of the residue in D_2O is then performed. The percent conversion of maleic anhydride to carboxymethyloxysuccinate equals 100× [ratio of the area of the chemical shift for carboxymethyloxysuccinic acid at 2.6–3.3δ (2H) to the sum of the areas for the chemical shifts for unreacted maleic acid at approximately 6.3δ (2H), fumaric acid (which may form during reaction) at approximately 6.8δ (2H) and carboxymethyloxysuccinic acid at 2.6–3.3δ (2H)].

EXAMPLES 1–10

TRISODIUM CARBOXYMETHYLOXYSUCCINATE AS A DETERGENT BUILDER

[Washing conditions: Terg-O-Tometer; Dacron/cotton VCD cloth; 120° F.; 180 p.p.m. (2:1 Ca^{++}/Mg^{++}) water; 0.20% concentration of total formulation for Examples 1 and 2; 0.25%. Concentration for Examples 3 to 10; pH=10.0]

Component	Formulation for Example— 1	2	3	4	5	6	7	8	9	10
Trisodium salt of carboxymethyloxysuccinic acid, percent	50		50		50		50		50	
STPP, percent		50		50		50		50		50
RU silicate solids, percent	10	10	10	10	10	10	10	10	10	10
LAS, percent	18	18								
Neodol 45-11, percent			10	10						
C_{14}–C_{16} HAMT, percent					18	18				
Sulfobetaine DCH, percent							18	18		
Sodium C_{15}–C_{18} α-olefin sulfonate, percent									18	18
Water, percent	Balance	Balance	Balance	Balance	Balance	Balance	Balnace	Balance	Balance	Balance
Average detergency (DU's)	23.0	24.3	21.6	24.1	19.7	24.1	23.5	24.3	22.6	24.9
Percent efficiency vs. control formulation [1]	95		90		82		97		91	

[1] I.e., 1 vs. 2; 3 vs. 4; 5 vs. 6; 7 vs. 8; and 9 vs. 10.

EXAMPLE 11

A machine dishwashing composition is prepared with the following materials:

	Percent
Trisodium salt of carboxymethyloxysuccinic acid	43.0
Chlorinated trisodium phosphate	21.0
N silicate solids (3.22 SiO_2/Na_2O ratio)	14.0
RU silicate solids	12.0
Pluronic L62 (a nonionic surfactant sold by Wyandotte Chemical Corporation which is an ethylene oxide condensate of a polyoxypropylene glycol)	2.5
Sodium sulfate	4.7
Water	2.8

The above formula has acceptable dishwashing properties which are similar to those of the same formula containing sodium tripolyphosphate in place of the trisodium carboxymethyloxysuccinate.

The procedure of Example 15 is repeated except the mixture is refluxed for thirty minutes as opposed to two hours and the pH of the solution obtained after filtering off the $CaCO_3$ is adjusted to 8.6 with 10% sulfuric acid. Yields of about 93% are obtained.

EXAMPLE 17

The reaction mixture from Example 15 is cooled and before treatment with sodium carbonate, the intermediate calcium chelate salt is isolated by filtration (percent Ca calculated for $C_6H_5O_7Ca_{1.5}\cdot H_2O$, 22.5; found, 22.9). The product is then decalcified by treatment of an aqueous slurry of the product with a cation-exchange resin followed by filtration and evaporation of the filtrate. The residue of carboxymethyloxysuccinic acid solidifies on cooling to a crystalline mass, M.P. 112–113° C. The acid is then converted into a salt by partial or complete neutralization with sodium hydroxide to form mono-, di- or trisodium carboxymethyloxysuccinate.

EXAMPLES 18–22

In place of the calcium hydroxide of Example 15, the divalent metal hydroxides $Mg(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$ and $Zn(OH)_2$ are used.

Using $Mg(OH)_2$ in the reaction of Example 15 with 200 ml. of water in place of 100 ml. of water and at an initial pH of 9 (measured at room temperature) gives a 79% conversion of maleic anhydride into product after 17 hours refluxing at 100° C.

Similarly with $Sr(OH)_2$ at initial pH of 11.5 (measured at room temperature), the conversion is 88% in four hours at 100° C. With $Ba(OH)_2$ at initial pH of 10–11, the conversion is 54% after ten hours at 100° C. With $Zn(OH)_2$ and at an initial pH of 8, a 47% conversion is obtained after nine hours at 100° C. With $Ca(OH)_2$ at initial pH of 11, the conversion is 91.5% in less than 15 minutes at 150° C. The speed of the reaction with $Ca(OH)_2$ makes it feasible for the process to be run continuously.

EXAMPLES 23–28

The procedure of Example 15 is repeated except that 200 ml. of water is used and the amount of calcium hydroxide used is sufficient to obtain the following pH's as measured initially at room temperature.

Example	pH	Percent conversion of maleic anhydride to trisodium carboxymethyloxysuccinate after two hours refluxing
23	10.2	10
24	10.5	9
25	11.0	52
26	11.3	97
27	11.6	91
28	12.1	81

EXAMPLE 29

The procedure of Example 15 is repeated except the 200 ml. of water is used and 27.5 g. of zinc oxide (.338 mole) is used in place of 27.0 g. of calcium hydroxide to adjust the pH to about 8.0. The percent conversion of maleic anhydride to trisodium carboxymethyloxysuccinate after two hours refluxing is 41% as determined NMR analysis.

EXAMPLES 30–31

The procedure of Example 15 is repeated except that .21 mole of glycolic acid is used instead of .24 mole. The amount of calcium hydroxide used is 24 g. (.324 mole). After two hours reflux at 100° C., the conversion of maleic acid to carboxymethyloxysuccinate is 93% based on NMR analysis.

The procedure of Example 15 is repeated except that the reaction mixture is heated at 60° C. for two hours. The conversion of maleic anhydride to carboxymethyloxysuccinate is 88%.

EXAMPLE 32

The procedure of Example 15 is repeated except the pH is adjusted to 12.0 and the reaction mixture is refluxed for 15 minutes. The conversion of maleic acid to carboxymethyloxysuccinate is 90% based on NMR analysis.

At high pH and continued refluxing, the carboxymethyloxysuccinate product formed may undergo a retro-Michael reaction giving rise to the fumarate salt.

Referring to Examples 33–36, it has been determined that by increasing the level of the surfactants used in the detergent formulations and particularly the anionic and zwitterionic actives, the detergency of the formulations are enhanced. It has also been found that LAS and alpha-olefin sulfonate salts are very effective for this purpose.

Examples 33–36 clearly demonstrate that when the levels of LAS are increased, the detergency of the formulation is enhanced significantly when compared to a standard LAS/tripolyphosphate formulation. When using other actives, similar effects are observed.

EXAMPLES 33–36

TRISODIUM CARBOXYMETHYLOXYSUCCINATE AS A DETERGENT BUILDER WITH VARIOUS LEVELS OF AN ANIONIC SURFACTANT

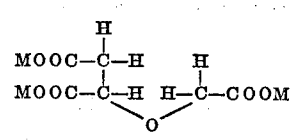
[Washing conditions: Terg-O-Tometer; Dacron/cotton VCD cloth; 120° F; 180 p.p.m. (2:1 Ca^{++}/Mg^{++}) water; 0.2% concentration of total formulation; pH=10.0]

Component	Formulation for Example— 33	34	35	36
Trisodium salt of carboxymethyloxysuccinic acid, percent	50	50	50	----------
STPP, percent	----------	----------	----------	50
RU silicate solids, percent	10	10	10	10
LAS, percent	18	27	36	81
Water	Balance	Balance	Balance	Balance
Average detergency (DU's)	22.6	24.4	24.7	22.7
Percent efficiency vs. standard formulation	100	107	109	----------

It is intended to cover all changes and modifications of the preferred embodiments of the invention, herein chosen for the purpose of illustration, which do not constitute departures form the spirit and scope of the invention.

What is claimed is:

1. A detergent composition comprising (1) a water-soluble organic detergent compound selected from the group consisting of anionic, nonionic, zwitterionic and ampholytic detergent compounds and (2) a builder salt having the general formula:



wherein M is selected from the group consisting of alkali metal, ammonium and substituted ammonium cations and combinations thereof, the weight ratio of said builder salt to detergent compound ranging from about 1:20 to 50:1.

2. The detergent composition as defined in claim **1** wherein said detergent composition contains sodium carbonate.

3. The detergent composition as defined in claim **1** wherein the organic detergent is alpha olefin sulfonate having a chain length from C_{15} to C_{18}.

4. The detergent composition as defined by claim **1** wherein the weight ratio of the builder salt to detergent compound ranges from about 1:20 to about 20:1.

5. The detergent composition as defined by claim 1 wherein the carboxymethyloxysuccinate is trisodium carboxymethyloxysuccinate.

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MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

252—132, 142, 156, 180, 546; 210—58; 260—535 P

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,692,685
DATED : September 19, 1972
INVENTOR(S) : Lamberti, et al.

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

Col. 2, line 13: delete the phrase "R is H or $-CH_2COOM$ and".

Col. 2, line 19: delete the "comma" after the word "tri-ammonium".

Col. 2, line 43: add a -- comma -- after the word "oxydi-succinate".

Col. 5, line 9: change "1-18" to -- 1-14 --.

Col. 7, line 61: change "the" (last word in line) to -- that --.

Col. 7, line 66: insert the word -- by -- between "determine" and "NMR".

Col. 8, line 37: In Table, Example 36: change "81" to -- 18 --.

Signed and Sealed this

Twenty-fifth Day of *September 1979*

[SEAL]

Attest:

Attesting Officer

LUTRELLE F. PARKER
Acting Commissioner of Patents and Trademarks