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Rapko

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[54] SALTS OF TETRAHYDROFURAN
POLYCARBOXYLIC ACIDS AS
DETERGENT BUILDERS AND
COMPLEXING AGENTS

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Related U.S. Application Data

[62] Division of Ser. No. 385,131, Aug. 2, 1973, Pat. No. 3,835,163.

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252/132; 252/135; 252/180; 252/DIG. 11

[51] Int. Cl.² C11D 7/54

[58] Field of Search 252/89, 97, 99, 132, 135,
252/180, DIG. 11; 260/347.3, 347.5

[56] References Cited

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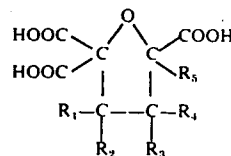
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[57] ABSTRACT

Salts of tetrahydrofuran polycarboxylic acids represented by the formula



wherein R_1 , R_2 , R_3 , R_4 and R_5 are hydrogen or carboxylic acid groups, at least one of R_1 , R_2 , R_3 and R_4 being a carboxylic acid group when R_5 is a carboxylic acid group are useful as complexing agents and/or detergency builders. The ester forms of such compounds, as well as the acids are useful as intermediates for production of the salts.

16 Claims, No Drawings

SALTS OF TETRAHYDROFURAN POLYCARBOXYLIC ACIDS AS DETERGENT BUILDERS AND COMPLEXING AGENTS

This is a division of application Ser. No. 385,131, filed Aug. 2, 1973, now U.S. Pat. No 3,835,163.

BACKGROUND OF THE INVENTION

This invention relates to novel tetrahydrofuran polycarboxylic acids and salts useful as complexing agents and detergency builders; to detergent formulations containing such compounds and to ester forms of such compounds useful, inter alia, as intermediates for preparation of the salts and acids.

The utility of compounds characterized by the ability to complex various metal and alkaline earth metal ions (particularly ions such as calcium ions which contribute to "hardness" of water) in aqueous media and/or provide, in combination with various detergent surfactants, detergent formulations of enhanced cleansing ability is well recognized by those skilled in the art. Such compounds are used in water treating applications (e.g. to "soften" water) and/or as detergency builders.

Although many compounds having complexing and/or detergency builder functionality are known the provision of novel compounds composed of only carbon, hydrogen and oxygen and having such functionality is desirable.

Since most known complexing agents form complexes with water hardness ions on a 1:1 mole basis, novel compounds having the ability to complex greater quantities of such ions are particularly desired.

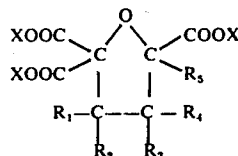
SUMMARY OF THE INVENTION

It is an object of this invention to provide novel compounds useful as complexing agents and/or detergency builders and intermediates for the synthesis of such compounds. A further object of the invention is to provide novel detergent formulations containing the builder compounds of this invention.

The compounds of this invention are tetrahydrofuran polycarboxylic acids, their salts and esters whose structure, synthesis, and use will be understood from the following description of the preferred embodiments.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compounds of the present invention are represented by the formula



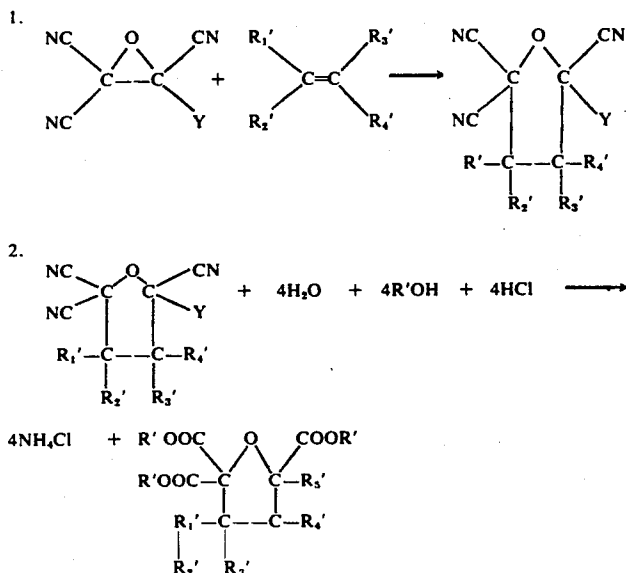
wherein X is hydrogen, alkali metal, ammonium, alcohol ammonium, (wherein the alkyl group contains from 1 to 4 carbon atoms) or an alkyl group containing from 1 to 20 carbon atoms (it is not necessary that all X groups in the compound be identical) and R_1 , R_2 , R_3 , R_4 and R_5 are hydrogen or $-\text{COOX}$. At least one of the R_1 , R_2 , R_3 and R_4 groups must be $-\text{COOX}$ when R_5 is COOX . Thus, the formula is seen to encompass acid, salt and ester compounds. It is further apparent that certain of the compounds, for example, those in which R_1 and R_4 are $-\text{COOX}$ and R_2 and R_3 are hydrogen include both cis and trans configurations.

The salt forms of the compounds of this invention are useful as complexing agents and/or as detergency builders.

Tetrahydrofuran-2,2,3,4,5,5-hexacarboxylate salts, especially in the trans configurations and preferably the pentasodium salts, are preferred compounds of the invention in view of their ability to complex more than one mole of calcium ion per mole of hexacarboxylate salt.

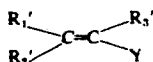
The ester forms of the compounds of this invention are useful as intermediates for preparation of the salt forms as will be apparent from the subsequent description of methods of preparing compounds of this invention. In addition, certain of the esters (particularly those having more than 4 carbon atoms in the ester alkyl groups) will be found to exhibit plasticizer properties or, in the case of the higher alkyl (9 to 20 carbon atoms) esters, surfactant properties.

The ester forms of the compounds of this invention can be prepared by reactions represented by the equations:



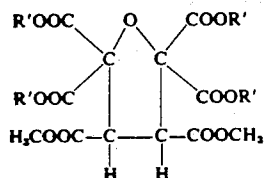
In the formulae of the above equations Y is hydrogen or CN, R_1' , R_2' , R_3' , R_4' and R_5' are hydrogen or COOR, at least one of R_1' , R_2' , R_3' and R_4' being COOR when R_5' is COOR and R and R' are alkyl groups containing from 1 to 20 carbon atoms.

The number and position of carboxylate groups in the ester product is determined by the choice of the



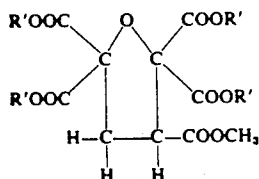
compound.

For example: the use of dimethyl maleate will yield a mixture of the cis and trans configurations of

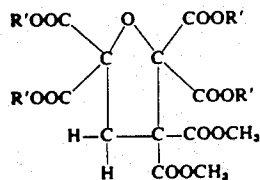


whereas the use of dimethyl fumarate will yield the trans form of this compound.

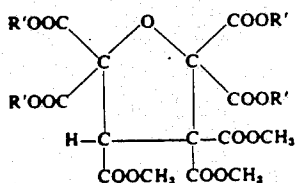
The use of methyl acrylate will yield



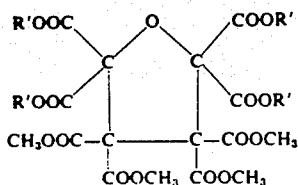
The use of methylene malonic ester $\text{CH}_2 = \text{C}(\text{COOCH}_3)_2$ will yield



The use of ethene 1,1,2 trimethylcarboxylate will yield



The use of ethene 1,1,2,2 tetramethylcarboxylate yields



Higher esters are obtained by use of higher alkyl carboxylate esters in the reaction or by transesterifying the lower esters with the appropriate alcohol. The R' in the COOR' groups occupying the 2,2,5,5 positions corresponds to the R' in the alcohol (R'OH) used in the second reaction.

The reaction shown in the first equation can be conveniently conducted in an inert solvent, e.g., 1,2-dibromoethane, at a temperature sufficiently high to promote a reasonable rate of reaction, e.g. about 120°C in the case of dimethyl fumarate. Preferably, the reaction is conducted under reflux and a nitrogen blanket to prevent volatilization or oxidation of the reactants. The product is recovered by conventional crystallization and filtration techniques. Reactions of this general type are fully understood by those skilled in the art, and are discussed, for example, in U.S. Pat. No. 3,317,567.

The alcoholysis reaction shown in the second equation is preferably conducted by mixing the product of the first reaction with the requisite amount of water and alcohol cooling to about 0° to 40°C; adding gaseous HCl; filtering to remove NH_4Cl ; adding concentrated sulfuric acid as a catalyst and refluxing to complete the reaction.

The corresponding alkali metal salts are readily obtained by conventional saponification techniques (using less than stoichiometric amounts of alkali metal hydroxide if a partial salt such as the preferred pentasodium tetrahydrofuran 2,2,3,4,5,5-hexacarboxylate is desired). The corresponding ammonium and alkanol ammonium salts are more easily obtained by neutralization of the acid forms of the compounds of this invention.

Acidulation of the salt with a strong acid, e.g., HCl, H_2SO_4 , or a strong acid ion exchange resin, will yield the acid forms of the compounds of this invention.

The tetrahydrofuran polycarboxylate salts of this invention are useful as agents for complexing metal and/or alkaline earth metal ions in aqueous media. The amount of polycarboxylate required to effectively complex the ions in a given system will depend, to some extent, on the particular polycarboxylate salt being used and the particular metal or alkaline earth metal ions in the aqueous media. Generally, complexing is more effective in basic solution. Optimum conditions and amounts of complexing agent can readily be determined by routine experimentation.

The tetrahydrofuran polycarboxylate salts are also useful as builders in detergent formulations. Generally, the use of the alkali metal salts, particularly the sodium salt is preferred. However, in some formulations (such as liquid formulations where greater builder solubility is required) the use of ammonium or alkanol ammonium salts may be desirable.

The detergent formulations of this invention will contain at least 1% by weight and preferably at least 5% by weight of the polycarboxylate salts of this invention. In order to obtain the maximum advantages of the builder compositions of this invention, the use of from 5 to 75% of these polycarboxylate salts is particularly preferred. The tetrahydrofuran polycarboxylic salt compounds of this invention can be the sole detergency builder or these compounds can be utilized in combination with other detergency builders which may constitute from 0 to 95% by weight of the total builders in the

formulation. By way of example, builders which can be employed in combination with the novel builder compounds of this invention include water soluble inorganic builder salts such as alkali metal polyphosphates, i.e., the tripolyphosphates and pyrophosphates, alkali metal carbonates, borates, bicarbonates and silicates and water soluble organic builders including amino polycarboxylic acids and salts such as alkali metal nitrilotriacetates, cycloalkane polycarboxylic acids and salts, ether polycarboxylates, alkyl polycarboxylates, epoxy polycarboxylates, other tetrahydrofuran polycarboxylates such as 1,2,3,4 or 2,2,5,5 tetrahydrofuran tetracarboxylates, benzene polycarboxylates, oxidized starches, amino (trimethylene phosphonic acid) and its salts, diphosphonic acids and salts (e.g., methylene diphosphonic acid; 1-hydroxy ethylidene diphosphonic acid) and the like.

The detergent formulations of this invention will generally contain from 5 to 95% by weight total builder (although greater or lesser quantities may be employed if desired) which, as indicated above, may be solely the tetrahydrofuran polycarboxylic acids and/or salts compounds of this invention or mixtures of such compounds with other builders. The total amount of builder employed will be dependent on the intended use of the detergent formulation, other ingredients of the formulation, pH conditions and the like. For example, general laundry power formulations will usually contain 20 to 60% builder; liquid dishwashing formulations 11 to 12% builder; machine dishwashing formulations 60 to 90% builder. Optimum levels of builder content as well as optimum mixtures of builders of this invention, with other builders for various uses can be determined by routine tests in accordance with conventional detergent formulation practice.

The detergent formulations of this invention will generally contain a water soluble detergent surfactant although the surfactant ingredient may be omitted from machine dishwashing formulations. Any water soluble anionic, nonionic, zwitterionic or amphoteric surfactant can be employed.

Examples of suitable anionic surfactants include soaps such as the salts of fatty acids containing about 9 to 20 carbon atoms, e.g. salts of fatty acids derived from coconut oil and tallow; alkyl benzene sulfonates--particularly linear alkyl benzene sulfonates in which the alkyl group contains from 10 to 16 carbon atoms; alcohol sulfates; ethoxylated alcohol sulfates; hydroxy alkyl sulfonates; alkyl sulfates and sulfonates; mono-glyceride sulfates; acid condensates of fatty acid chlorides with hydroxy alkyl sulfonates and the like.

Examples of suitable nonionic surfactants include alkylene oxide (e.g., ethylene oxide) condensates of mono and polyhydroxy alcohols, alkyl phenols, fatty acid amides, and fatty amines; amine oxides; sugar derivatives such as sucrose monopalmitate; long chain tertiary phosphine oxides; dialkyl sulfoxides; fatty acid amides, (e.g., mono or diethanol amides of fatty acids containing 10 to 18 carbon atoms), and the like.

Examples of suitable zwitterionic surfactants include derivatives of aliphatic quaternary ammonium compounds such as 3-(N,N-dimethyl-N-hexadecyl ammonio) propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxy propane-1-sulfonate.

Examples of suitable amphoteric surfactants include

betains, sulfobetains and fatty acid imidazole carboxylates and sulfonates.

It will be understood that the above examples of surfactants are by no means comprehensive and that numerous other surfactants are known to those skilled in the art. It will be further understood that the choice and use of surfactants will be in accordance with well understood practices of detergent formulation. For example, anionic surfactants, particularly linear alkyl benzene sulfonate are preferred for use in general laundry formulations, whereas low foaming nonionic surfactants are preferred for use in machine dishwashing formulations.

The quantity of surfactant employed in the detergent formulations of this invention will depend on the surfactant chosen and the end use of the formulation. In general, the formulations will contain from 5 to 50% surfactant by weight, although as much as 95% or more surfactant may be employed if desired. For example, general laundry powder formulations normally contain 5 to 50%, preferably 15 to 25% surfactant; machine dishwashing formulations 0.5 to 5%; liquid dishwashing formulations 20 to 45%. The weight ratio of surfactant to builder will generally be in the range of from 1:12 to 2:1.

In addition to builder and surfactant components, detergent formulations may contain fillers such as sodium sulfate and minor amounts of bleaches, dyes, optical brighteners, soil anti-redeposition agents, perfumes and the like.

In machine dishwashing compositions the surfactant will be a low-foaming anionic surfactant which will constitute 0 to 5% of the formulation.

The term "low-foaming" surfactant connotes a surfactant which, in the foaming test described below, reduces the revolutions of the washer jet-spray arm during the wash and rinse cycles less than 15%, preferably less than 10%.

In the foaming test, 1.5 grams of surfactant is added to a 1969 Kitchen-Aid Home Dishwasher, Model No. KOS-16, manufactured by Hobart Manufacturing Company which is provided with means for counting revolutions of the washer jet-spray arm during wash and rinse cycles. The machine is operated using distilled water feed at a machine entrance temperature of 40°C. The number of revolutions of the jet-spray arm during the wash and rinse cycles is counted. The results are compared with those obtained by operation of the machine using no surfactant charge and percentage decrease in number of revolutions is determined.

The surfactant should, of course, be compatible with the chlorine containing component hereinafter discussed. Examples of suitable nonionic surfactants include ethoxylated alkyl phenols, ethoxylated alcohols (both mono- and di-hydroxy alcohols), polyoxyalkylene glycols, aliphatic polyethers and the like. The widely commercially utilized condensates of polyoxypropylene glycols having molecular weights of from about 1,400 to 2,200 with ethylene oxide (the ethylene oxide constituting 5 to 35 weight percent of the condensate) are, for example, advantageously used in the machine dishwashing formulations of this invention.

Suitable low-foaming anionic surfactants include alkyl diphenyl ether sulfonates such as sodium dodecyl diphenyl ether disulfonates and alkyl naphthalene sulfonates.

Mixtures of suitable low-foaming surfactants can be utilized if desired.

In addition, machine dishwashing formulations will contain sufficient chlorine providing compound to provide 0.5 to 2% available chlorine. For example, the formulation may contain from 0.5 to 5%, preferably 1 to 3% of a chlorocyanurate or from 10 to 30% chlorinated trisodium phosphate. Suitable chlorocyanurates are sodium and potassium dichlorocyanurate; [(monotrichloro) tetra-(mono potassium dichloro)] penta-isocyanurate; (mono-trichloro) (monopotassium dichloro) di-isocyanurate.

Machine dishwashing compositions should additionally contain from 5 to 30% soluble sodium silicate having an SiO_2 to Na_2O mole ratio of from 1:1 to 3.2:1 preferably about 2.4:1 to inhibit corrosion of metal parts of dishwashing machines and provide over-glaze protection to fine china.

Machine dishwashing compositions will generally contain at least 10%, preferably at least 20% builder, up to a maximum of about 90% builder. The new builder compounds of this invention should constitute at least 5% of the weight of the machine dishwashing formulation in order to obtain the full effects of their inherent characteristics.

The invention is further illustrated by the following examples which deal with the preparation and use of the particularly preferred tetrahydrofuran 2,2-trans-3,4,5,5-hexacarboxylate compounds. It will be recognized by those skilled in the art that other compounds of this invention can be prepared and utilized in a similar manner pursuant to the preceding discussion. In the examples, all parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

Tetracyanoethylene oxide (56.6 grams); dimethyl fumarate (56.6 grams); ethylene dibromide solvent (450 ml.) are maintained at about 120°C with stirring for about 22 hours under nitrogen atmosphere in a glass flask fitted with a reflux condenser. A dark brown solution forms which is filtered while hot to remove minor amounts of unidentified solid impurities. The filtrate is dried on a rotary evaporator and the residue washed with diethylether and dried under nitrogen. The residue product is purified by dissolution in and crystallization from methyl alcohol followed by vacuum drying. The identity of the product as dimethyl tetrahydrofuran-trans-3,4-dicarboxylate-2,2,5,5-tetranitrile is confirmed by elemental analysis and a H nuclear magnetic resonance spectrum in deuterated acetone in which the 3 and 4 protons appear as a singlet at 5.45 ppm; the ester CH_3 protons as a singlet at 4.10 ppm vs. TMS (relative areas 1:3).

Ninety grams of the dimethyl tetrahydrofuran-trans-3,4-dicarboxylate-2,2,5,5-tetranitrile; 21 grams water; 1,000 ml. methyl alcohol are charged to a glass flask and the temperature of the mixture is held between 0° to 40°C while 50 grams of hydrogen chloride gas is bubbled into the mixture. The reaction mixture is filtered to remove ammonium chloride; 1.5 ml. concentrated sulfuric acid is added as catalyst to the filtrate which is then refluxed for about 30 hours. Upon cooling, solid product separates from the solution and is removed by filtration. The solid is dissolved in chloroform; washed with 5% sodium bicarbonate and water. The chloro-

form solution is dried over magnesium sulfate and the chloroform evaporated to leave an oily residue. Dissolution of the residue in methanol followed by crystallization yields a pure crystalline product. The identity of the product as hexamethyl tetrahydrofuran 2,2-trans-3,4,5,5 hexacarboxylate is confirmed by elemental analysis and a H nuclear magnetic resonance spectrum in deuterated chloroform which exhibits a singlet at 4.50 ppm corresponding to the 3 and 4 protons; a singlet at 4.02 ppm corresponding to the two CH_3 ester groups at the 3 and 4 positions; a singlet at 3.88 ppm corresponding to the four ester CH_3 groups at the 2 and 5 positions (relative areas 1:3:4).

EXAMPLE II

A mixture of 55.4 grams 50% sodium hydroxide; 100 ml. water; 48.5 grams hexamethyl tetrahydrofuran 2,2-trans-3,4,5,5 hexacarboxylate is heated under reflux at 90°C for 24 hours in a glass flask. The solution is concentrated by distillation of methanol and water from the flask. The reaction mixture is cooled to room temperature and product precipitated by addition of 1,000 ml. methanol. The identity of the product as pentasodium monohydrogen tetrahydrofuran 2,2-trans-3,4,5,5 hexacarboxylate is confirmed by chemical analysis and a H nuclear magnetic resonance spectrum in deuterium oxide exhibiting a singlet at 4.1 ppm.

EXAMPLE III

Pentasodium monohydrogen tetrahydrofuran 2,2-trans-3,4,5,5 hexacarboxylate (289.2 mg.) is dissolved in 10 ml. deionized water and passed through a column packed with a strong acid ion exchange resin (sulfonated polystyrene marketed by Fisher Scientific Company under the trademark Rexyn 101). This procedure yields tetrahydrofuran 2,2-trans-3,4,5,5 hexacarboxylic acid. The titration curve of the acid with sodium hydroxide exhibits three breaks and indicates that four protons are highly acidic (apparent pK_a 's equal to or less than 5.7); a fifth proton is less acidic (apparent pK_a of about 6.8); and the sixth proton has an apparent pK_a of about 9.1.

EXAMPLE IV

Pentasodium monohydrogen tetrahydrofuran 2,2-trans-3,4,5,5 hexacarboxylate is tested for sequestration function using the procedures described by Matzner et al. "Organic Builder Salts as Replacements for Sodium Tripolyphosphate" Tenside Detergents, 10, Heft 3, pages 119 through 125 (1973). In this test, the divalent ion electrode shows two separate end points for titration of calcium ion with a solution of the hexacarboxylate salt. This is due to the formation of 2:1 and 1:1 (Ca^{++} /ligand) complexes. The average sequestration values (intensity multiplied by capacity expressed as a percentage of sodium tripolyphosphate sequestration value are in the range of 138 to 188% depending upon the complex formed.

EXAMPLE V

Detergent formulations containing the percent builder shown in Table I below; 17% linear alkylbenzene sulfonate having an average molecular weight of about 230; 12% sodium silicate; remainder, sodium sulfate are prepared. The formulations are tested by washing identically soiled fabric swatches (indicated in the

table) in water of 200 ppm hardness at 40°C containing 0.15% detergent formulation using identical washing techniques. The reflectivity of the soiled swatches before and after washing is measured instrumentally and the difference reported in Table I as Δ Rd. High Δ Rd values are indicative of correspondingly high detergent effectiveness.

TABLE I

Builder	Cotton Fabric — Δ Rd			Polyester/Cotton Fabric — Rd		
	50% Builder	37.5% Builder	25% Builder	50% Builder	37.5% Builder	25% Builder
Pentasodium monohydrogen tetrahydrofuran 2,2-trans-3,4,5,5-hexacarboxylate	28.7	27.1	21.3	13.5	10.1	9.8
Sodium Tripolyphosphate	26.2	19.0	14.5	12.0	8.7	5.7

EXAMPLE VI

Three pentasodium monohydrogen tetrahydrofuran 2,2-trans-3,4,5,5-hexacarboxylate built detergent formulations corresponding to those shown in Example V except that linear alkylbenzene sulfonate surfactant is replaced with:

1. a nonionic surfactant - a condensate of 7 molecular proportions of ethylene oxide with linear secondary alcohols containing 11 to 15 carbon atoms
2. an amphoteric surfactant - sodium hydroxyalkyl (alkyl group contains an average of 15 carbon atoms) N-methyl taurate
3. a zwitterionic surfactant -cocodimethylsulfopropylbetaine

are prepared and tested. All three formulations exhibit effective detergency.

EXAMPLE VII

A machine dishwashing formulation containing 50% pentasodium monohydrogen tetrahydrofuran 2,2-trans-3,4,5,5-hexacarboxylate; 35% of an aqueous solution containing 47% sodium silicate having an SiO_2 to Na_2O mole ratio of 2.4; 3% of a condensate of ethylene oxide with polyoxypropylene glycol marketed by Wy-

andotte Chemical Corporation as Pluronic L-62; 1.2% potassium dichlorocyanurate; 10.8% sodium sulfate is prepared. The formulation is used to wash soiled dishes and glassware in a conventional automatic home dish-

washing machine. Excellent cleaning is obtained and, in particular, the glassware is found substantially free from filming and spotting.

EXAMPLE VIII

Three machine dishwashing formulations are prepared which are identical to that of Example VII except

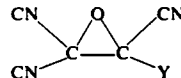
that the following surfactants are substituted for the ethylene oxide-polyoxypropylene glycol:

1. condensate of an internal, vicinal, linear diol having an average chain length of 16 carbon atoms with 3 molecular proportions of ethylene oxide
2. condensate of N-decanol with 2-½ molecular proportions ethylene oxide
3. sodium decyldiphenyl ether disulfonate.

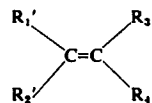
All three formulations provide excellent performance in cleaning dishes and glassware in a conventional automatic home dishwashing machine.

Other compounds of this invention can be prepared by techniques similar to those disclosed in Example I.

For example, Table II, below, indicates the esters which are obtained by reaction of various



compounds with various



compounds followed by alcoholysis with methanol.

TABLE II

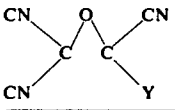
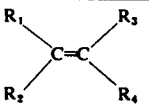
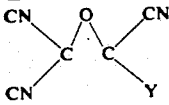
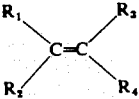
		Product
tetracyano ethylene oxide	dimethyl malonate	mixtures of hexamethyl tetrahydrofuran 2,2-cis-3,4,5,5 hexacarboxylate and hexamethyl 2,2-cis-3,4,5,5 hexacarboxylate
tetracyano ethylene oxide	methyl acrylate	pentamethyl tetrahydrofuran-2,2,3,5,5-pentacarboxylate
tetracyano ethylene oxide	dimethyl/methylene malonate	hexamethyl tetrahydrofuran-2,2,3,3,5,5-hexacarboxylate
tetracyano ethylene oxide	trimethyl ethene-1,1,2-tricarboxylate	heptamethyl tetrahydrofuran-2,2,3,3,4,5,5-heptacarboxylate
tetracyano ethylene oxide	tetramethyl ethene-1,1,2,2-tetracarboxylate	octamethyl-tetrahydrofuran-2,2,3,3,4,4,5,5-octacarboxylate
tricyano ethylene oxide	ethylene	trimethyl-tetrahydrofuran-2,2,5-tricarboxylate
tricyano ethylene oxide	methyl acrylate	mixture of cis and trans tetramethyl tetrahydrofuran-2,2,3,5 and 2,2,4,5 tetracarboxylates
tricyano ethylene oxide	dimethyl methylene malonate	mixture of penta methyl tetrahydrofuran-2,2,3,3,5 and 2,2,4,4,5 penta carboxylate
tricyano ethylene oxide	dimethyl fumarate	mixture of pentamethyl tetrahydrofuran-2,2,-trans-3-cis-4,5 and 2,2-cis-3,5-trans-4

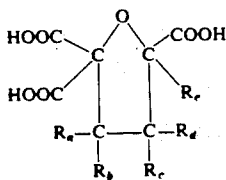
TABLE II-continued

		Product
tricyano ethylene oxide	dimethyl maleate	pentacarboxylate mixture of pentamethyl tetrahydrofuran-cis-2,2,3,4,5 and 2,2-cis-3,4-trans-5
tricyano ethylene oxide	trimethyl ethene-1,1,2-tricarboxylate	pentacarboxylate mixture of cis and trans-hexamethyl tetrahydrofuran-2,2,3,3,4,5 and 2,2,3,4,4,5 hexacarboxylate
tricyano ethylene oxide	tetramethyl ethene-1,1,2,2-tetracarboxylate	heptamethyl tetrahydrofuran-2,2,3,3,4,4,5 heptacarboxylate

Acids corresponding to the esters shown in Table II, above, and their corresponding totally or partially neutralized salts can be prepared by saponification and acidulation techniques comparable to those exemplified in Examples II and III.

What is claimed is:

1. A detergent formulation comprising (a) from 1 to 95% by weight of an alkali metal, ammonium or alkanol ammonium salt of a compound represented by the formula



wherein R_a , R_b , R_c , R_d , and R_e are selected from the group consisting of hydrogen and COOH, at least one of R_a , R_b , R_c and R_d being COOH when R_e is COOH and (b) from 0.5 to 95% by weight of a surfactant selected from the group consisting of water soluble anionic, nonionic, amphoteric and zwitterionic surfactants.

2. A formulation according to claim 1 containing from 5 to 75% of said salt.

3. A formulation according to claim 1 wherein R_a , R_d and R_e are COOH and R_b and R_c are hydrogen.

4. The formulation of claim 1 wherein said salt is pentasodium monohydrogen tetrahydrofuran 2,2,3,4,5,5-hexacarboxylate.

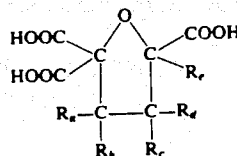
5. The formulation of claim 1 wherein said salt is pentasodium monohydrogen tetrahydrofuran 2,2-trans-3,4,5,5-hexacarboxylate.

6. The formulation of claim 1 wherein said salt is hexasodium tetrahydrofuran 2,2-trans-3,4,5,5-hexacarboxylate.

7. The formulation of claim 1 wherein said salt is hexasodium tetrahydrofuran 2,2-trans-3,4,5,5-hexacarboxylate.

8. A machine dishwashing composition comprising (a) from 0 to 5% by weight of a surfactant selected from the group consisting of low-foaming anionic and non-ionic surfactants and mixtures thereof, (b) a chlorine providing material selected from the group consisting of potassium dichlorocyanurate; sodium dichlorocyanurate; [(mono-trichloro) tetra-(monopotassium dichloro)] penta-isocyanurate; (mono-trichloro) (mono-potassium dichloro) diisocyanurate; chlori-

nated trisodium phosphate, said chlorine providing material being present in an amount sufficient to provide from 0.5 to 2% by weight available chlorine, (c) from 5 to 30% by weight soluble sodium silicate having an SiO_2 to Na_2O mole ratio of from 1:1 to 3.2:1 and (d) from 5 to 90% by weight of an alkali metal, ammonium or alkanol ammonium salt of a compound represented by the formula



wherein R_a , R_b , R_c , R_d and R_e are selected from the group consisting of hydrogen and COOH, at least one of R_a , R_b , R_c and R_d being COOH when R_e is COOM.

9. A formulation according to claim 8 containing from 20 to 75% of said salt.

10. A formulation according to claim 8 wherein R_a , R_d and R_e are COOH and R_b and R_c are hydrogen.

11. The formulation of claim 8 wherein said salt is pentasodium monohydrogen tetrahydrofuran 2,2,3,4,5,5-hexacarboxylate.

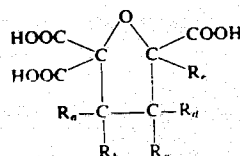
12. The formulation of claim 8 wherein said salt is pentasodium monohydrogen tetrahydrofuran 2,2-trans-3,4,5,5-hexacarboxylate.

13. The formulation of claim 8 wherein said salt is hexasodium tetrahydrofuran 2,2,3,4,5,5-hexacarboxylate.

14. The formulation of claim 8 wherein said salt is hexasodium tetrahydrofuran 2,2-trans-3,4,5,5-hexacarboxylate.

15. A formulation according to claim 8 containing at least 0.5% surfactant.

16. A method of complexing ions selected from the group consisting of metal ions and alkaline earth metal ions in an aqueous medium containing said ions by providing in said aqueous medium a quantity of an alkali metal, ammonium or alkanol ammonium salt of a compound represented by the formula



13

wherein R_a , R_b , R_c , R_d and R_e are selected from the group consisting of hydrogen and COOH, at least one of R_a , R_b , R_c and R_d being COOH when R_e is COOH,

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sufficient to form complexes with said ions.

* * * * *

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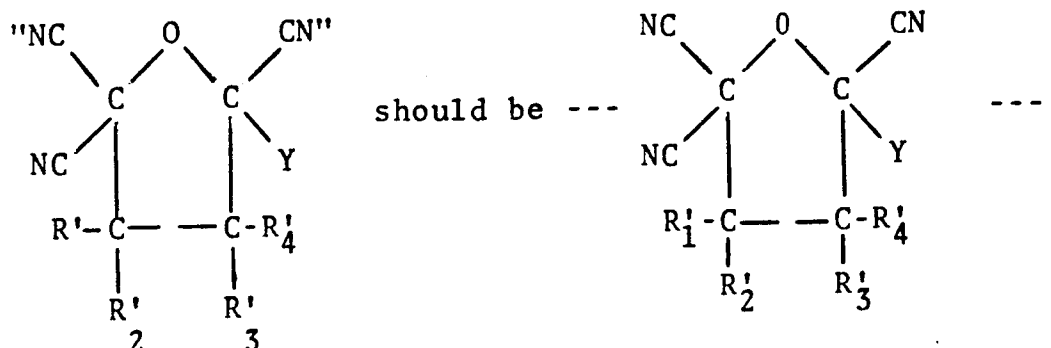
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252-77

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,923,679
 DATED : December 2, 1975
 INVENTOR(S) : John N. Rapko

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

Column 2, line 48, last structure of Equation 1:

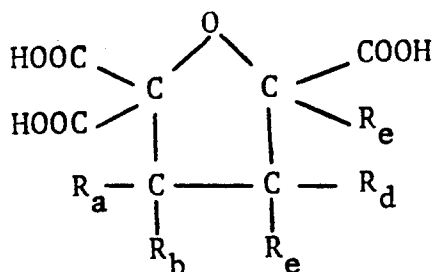


Columns 9 and 10, Table I, first line:

"Cotton Fabric - ΔRd Polyester/Cotton Fabric - Rd"

should be --- Cotton Fabric - Δ Rd Polyester/Cotton Fabric - ΔRd ---.

Column 12, line 62, "



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

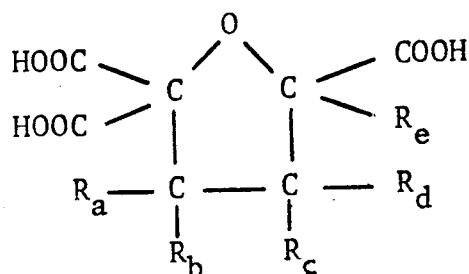
PATENT NO. 3,923,679

DATED December 2, 1975

INVENTOR(S) John N. Rapko

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

should be ---



Signed and Sealed this

sixth Day of April 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks