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⑤④ Detergency builders and built detergents.

⑤⑦ Detergent builder compositions comprise a mixture of tartrate succinate components and hydrocarbyl succinate components. The builder compositions provide detergent compositions which are especially useful for laundering fabrics.

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DETERGENCY BUILDERS AND BUILT DETERGENTS

Technical Field

The present invention relates to cleaning compositions which contain a mixture of succinate builders.

Background to the Invention

The literature is replete with reference to the ongoing search for new detergency builders, particularly those which are phosphorus-free. See, for example "Organic Builder: A review of Worldwise Efforts to Find Organic Replacements for Detergents Phosphates" Crutchfield JAOCS 55 58-65 (1978).

Polycarboxylated materials of various types have been suggested for use as detergency builders, and citric acid is currently used in some liquid laundry products. Other carboxylates are disclosed, for example in Stubbs et al; U.S. Patent 4,017,541; Issued April 12, 1977; Pearson et al; U.S. Patent 3,776,850; Issued December 4, 1973; Berg: U.S. Patent 3,120,207; Issued April 7, 1964 and Lamberti et al; U.S. Patent 3,635,830; Issued January 18, 1972.

The patent literature describes the use of alkyl-and alkenyl succinates as surfactants: US 2,283,214; detenency boosters UK 1,293,753; in various liquid cleaners UK 1,528171, US 4,277,378; builders US 2,462,758 and the like. See also US 3,784,486.

A variety of substituted succinates and "sulfur-succinates" are described for various similar uses: US 3,912,663, US 4,152,515 and US 3,725,286.

The use of ingredients succinates.in combination with certain detergency ingredients is also known; see EPO 79191 and EPO 70190, as well as German 32 05 791 and German 33 17 337.

Indeed, the use of carboxylate materials of various types in solid and liquid cleaners, is well-known; see UK 1,514,276 for amine soap mixture; UK 1,429,143 for zeolite/polycarboxylate mixtures: US 2,264,103 for citrate and other carboxylate plus soap mixtures; US 3,634,392 for polysaccharidic carboxylate detergency builders; US 3,898,187 for various sulfur-succinates in dish-washing detergents; and UK 1,400,898 for use with clay softeners.

Despite the heavy commitment of research towards the development of new detergency builders, there is a continuing search for improved technology in this area.

It is an object of this invention to provide detergency builders which are an improvement over the carboxylate builders of the literature.

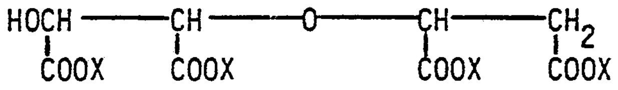
It is another object to provide detergent compositions, especially liquid laundry detergents, containing said improved builders.

Summary of the Invention

The present invention encompasses detergency builder compositions comprising:

(a) a tartrate succinate component which is a member selected from the group consisting of:

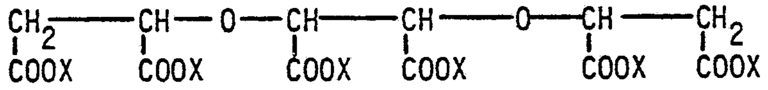
i)



$$\underset{COOX}{HOCH}-\underset{COOX}{CH}-O-\underset{COOX}{CH}-\underset{COOX}{CH_2}$$

wherein each X is H or a salt-forming cation;

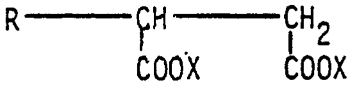
ii)



$$\underset{COOX}{CH_2}-\underset{COOX}{CH}-O-\underset{COOX}{CH}-\underset{COOX}{CH}-O-\underset{COOX}{CH}-\underset{COOX}{CH_2}$$

wherein each X is H or a salt-forming cation; and iii) mixtures therof; and

(b) a hydrocarbyl succinate component of the formula:



$$R-\underset{COOX}{CH}-\underset{COOX}{CH_2}$$

wherein R is a hydrocarbyl group and each X is H or a salt-forming cation.

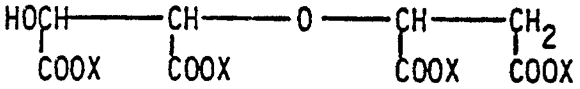
Preferred compositions are those wherein substituent R in the hydrocarbyl succinate component (b) is C_8-C_{18}, more preferably C_{12}-C_{16}, alkyl or alkenyl. 2-Dodecenyl succinic acid, or water-soluble salts thereof, is most preferred for use as component (b).

Typical compositions herein are those wherein the weight ratio of component (a):(b) is in the range of 15:1 to 1:15, more preferably 2:1 to 1:3.

This invention also encompasses detergent compositions comprising conventional detersive surfactants and detersive ingredients, and a detergency builder composition which comprises a mixture of:

(a) a tartrate succinate component which is a member selected from the group consisting of:

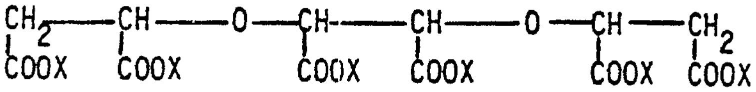
i)



$$HO\underset{COOX}{CH}-\underset{COOX}{CH}-O-\underset{COOX}{CH}-\underset{COOX}{CH_2}$$

wherein each X is H or a salt-forming cation;

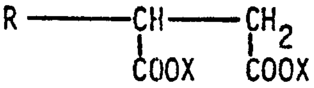
ii)



$$\underset{COOX}{CH_2}-\underset{COOX}{CH}-O-\underset{COOX}{CH}-\underset{COOX}{CH}-O-\underset{COOX}{CH}-\underset{COOX}{CH_2}$$

wherein each X is H or a salt-forming cation; and iii) mixtures therof; and

(b) a hydrocarbyl succinate component of the formula:



$$R-\underset{COOX}{CH}-\underset{COOX}{CH_2}$$

wherein R is a hydrocarbyl group and each X is H or a salt-forming cation.

Fully-formulated detergent compositions herein typically contain from 1% to 50% by weight of detersive surfactants and from 5% to 45% by weight of the detergency builder composition, the balance comprising conventional detergency ingredients or carriers. Conventional anionic, cationic, and nonionic detersive surfactants may be used in such compositions, as may other detersive surfactants as described more fully, hereinafter.

For laundry or hard-surface cleaning operations, such detergent compositions typically comprise:

I. A. from 0% to 30% by weight of an anionic detersive surfactant selected from the group consisting of conventional detersive alkyl benzene sulfonates, alkyl sulfates, alkyl ether sulfates soaps, and mixtures thereof; and

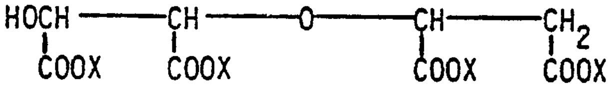
B. from 0% to 30% by weight of a nonionic detersive surfactant selected from the group consisting of conventional detersive ethoxylated alcohols, ethoxylated alkyl phenols, and mixtures thereof;

C. mixtures of A and B, with the proviso that the composition contains at least 5% by weight of detersive surfactant;

II. at least 10% by weight of a detergency builder component comprising:

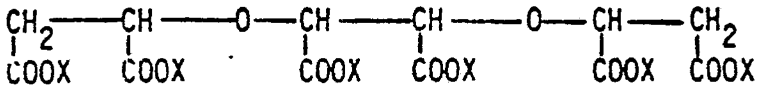
(a) i) a tartrate succinate component which is a member selected from the group consisting of:

i)



$$HO\underset{COOX}{CH}-\underset{COOX}{CH}-O-\underset{COOX}{CH}-\underset{COOX}{CH_2}$$

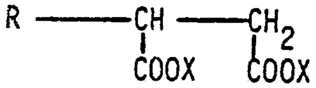
wherein each X is H or a salt-forming cation; and ii)



$$\underset{COOX}{CH_2}-\underset{COOX}{CH}-O-\underset{COOX}{CH}-\underset{COOX}{CH}-O-\underset{COOX}{CH}-\underset{COOX}{CH_2}$$

wherein each X is H or a salt-forming cation; iii) mixtures therof; and

(b) a hydrocarbyl succinate component of the formula:



$$R-\underset{COOX}{CH}-\underset{COOX}{CH_2}$$

wherein R is a hydrocarbyl group and each X is H or a salt-forming cation; preferably, the weight ratio of (a) to (b) in the range of 2:1 to 1:3; and

III. the balance of the composition comprising conventional detergent ingredients.

Preferred for laundry detergents are compositions wherein the hydrocarbyl succinate component of the builder is a C_{12}-C_{16} alkyl or alkenyl succinate; the compound 2-dodecenyl succinic acid, or water-soluble salts thereof, is most preferred.

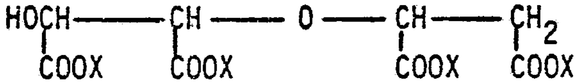
The compositions herein may be formulated as liquids; or formulated to be releasably carried on a sheet or other carrier substrate, or releasably contained in pouches; or formulated as bars, powders, granules, tablets, flowable gels, or the like.

All percentages, ratios or proportions herein are on a weight basis, unless otherwise specified.

Detailed Description of the Invention

The essential components of the builder compositions herein are the tartrate succinates and also the hydrocarbyl succinates, all as more fully described hereinafter. The detersive surfactants, optional detersive adjunct ingredients, as well as the carriers fillers, etc., used in the detergent compositions of this invention are all well-known to workers in this field.

(a) Tartrate Succinate Components: The tartrate succinate compounds used herein may be generically classified as "ether carboxylates." These include tartrate monosuccinic acid, or salts thereof, having the structural formula:



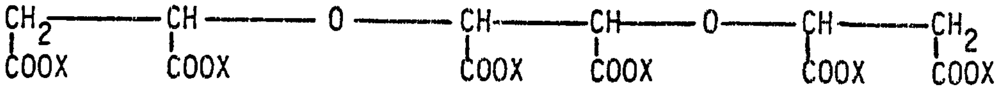
$$HO\underset{COOX}{CH}-\underset{COOX}{CH}-O-\underset{COOX}{CH}-\underset{COOX}{CH_2}$$

wherein each X is H or a salt-forming cation. This tartrate monosuccinic acid or salt thereof is hereinafter designated as "TMS." "TMS" is used to designate both the acid and salt forms of this material.

The tartrate monosuccinic acid component can be employed in the compositions herein in its free acid form, i.e., wherein X in the structural formula is H. Alternatively, and preferably this material may be partially or fully neutralized to a tartrate monosuccinate salt. Preferred salt-forming cations useful in forming the neutralized materials are those which yield substantially water-soluble salts of tartrate monosuccinic acid. Examples of such preferred salt-forming cations include alkali metal, e.g., sodium, potassium, lithium, ammonium, C_1-C_4 alkyl substituted ammonium and C_1-C_4 alkanolamine. The most preferred salt-forming cations are sodium, potassium, monoethanolamine and triethanolamine.

The tartrate monosuccinic component can be used in the builder compositions of this invention in an amount ranging from about 10% to 85% by weight of the builder. More preferably, the tartrate monosuccinate component will comprise from about 15% to 75% by weight of the builder compositions herein. Most preferably, this component is present to the extent of from about 50% to 65% by weight of the builder composition.

The second ether carboxylate composition which can be used in this invention is the particular novel polycarboxylate, tartrate disuccinic acid, or a salt thereof, having the structural formula:



$$\underset{\mathrm{COOX}}{\mathrm{CH_2}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH_2}}$$

wherein each X is H or a salt-forming cation. Tartrate disuccinic acid, or a salt thereof, is hereinafter designated as "TDS.".

As with TMS component, the TDS component can be utuilzed in either its free acid form or in its partially or fully neutralized form in the builder compositions herein. Neutralizing cations are likewise those which provide TDS in the form of its substantially water-soluble salt. Examples of suitable salt-forming cations include the same cations hereinbefore described for formation of the tartrate monosuccinate material. For convenience both the acid and salt forms of the TDS material will hereinafter be referred to as the "tartrate disuccinate" or "TDS" component.

The TDS component can be used in the builder compositions of this invention in an amount ranging from about 10% to 85% by weight of the builder. More preferably, the TDS component will comprise from about 15% to 75% by weight of the builder compositions herein. Most preferably, TDS is present to the extent of from about 50% to 65% by weight.

Mixtures of TMS and TDS can also be used; indeed, mixtures are generally obtained in the method of manufacture disclosed hereinafter. Typically, such mixtures comprise TMS:TDS in ratios ranging from 97:3 to 20:80. Preferred ratios TMS:TDS are 95:5 to 40:60. These are used at the same levels as mentioned above for the single components to provide the builder compositions of this invention.

(b)Hydrocarbyl Succinate Component: This component is of the general formual R-CH(COOH)CH_2-(COOH) i.e., derivatives of succinic acid, wherein R is hydrocarbyl, e.g., C_{10}-C_{20} alkyl or alkenyl, preferably C_{12}-C_{16} or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents, all as described in the above-mentioned patents.

These succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts, at levels of 15% to 90%, more preferably 35% to 50%, of the present builder compositions.

Specific examples of succinate builders include: lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenyl succinate (preferred), 2-pentadecenyl succinate, and the like.

(c) Detersive Surfactants: The detergent compositions of this invention will contain organic surface-active agents ("surfactants") to provide the usual cleaning benefits associated with the use of such materials.

Detersive surfactants useful herein include well-known synthetic anonic, nonionic, amphoteric and zwitterionic surfactants. Typical of these are the alkyl benzene sulfonates, alkyland alkylether sulfates, paraffin sulfonates, olefin sulfonates, amine oxides, alpha-sulfonates of fatty acids and of fatty acid esters, ethoxylated alcohols and ethoxylated alkyl phenols, and the like, which are well-known from the detergency art. In general, such detersive surfactants contain an alkyl group in the C_9-C_{10} range; the anionic detersive surfactants can be used in the form of their sodium, potassium or triethanolammonium salts. Standard texts such as the McCutcheon's Index contain detailed listings of such typical detersive surfactants. C_{11}-C_{14} alkyl benzene sulfonates, C_{12}-C_{18} paraffin-sulfonates and C_{11}-C_{18} alkyl sulfates are especially preferred in the compositions of the present type.

Aslo useful herein are the water-soluble soaps, e.g. the common sodium and potassium coconut or tallow soaps well-known in the art.

The surfactant component can comprise as little as 1% of the detergent compositions herein, but generally the compositions will contain 5% to 40%, preferably 6% to 30%, of surfactant. Mixtures of the anionics, such as the alkyl benzene sulfonates, alkyl sulfates and paraffin sulfonates, with C_9-C_{16} ethoxylated alcohol surfactants are preferred for through-the-wash cleansing of a broad spectrum of soils and stains from fabric.

(d) Detersive Adjuncts: The compositions herein can contain other ingredients which aid in their cleaning performance. For example, it is highly preferred that the laundry compositions herein also contain enzymes to enhance their through-the wash cleaning performance on a variety of soils and stains. Amylase and protease enzymes suitable for use in detergents are well-known in the art and in commercially available liquid and granular detergents. Commercial detersive enzymes (preferably a mixtures of amylase and protease) are typically used at levels of 0.001% to 2%, and higher, in the present compositions.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various other optional ingredients typically used in commerical produces to provide aesthetic or additional product performance benefits. Typical ingredients include pH regulants, perfumes, dyes, bleaches, optical brighteners, soil suspending agents, hydrotropes and gel-control agents, freeze-thaw stabilizers, bactericides, preservatives, suds control agents, bleach activators and the like.

In a through-the-wash fabric laundry mode, the compositions are typically used at a concentration of 500 ppm, preferably 0.10% to 2.5%, in an aqueous laundry bath, typically at pH 7-11 to launder fabrics. The laundering can be carried out by agitating fabrics with the present compositions over then range from 5°C to the boil, with excellent results.

Preparation of TMS/TDS

The TMS and TDS compounds used in the practice of this invention are not believed to be described in the literature, so their preparation will be described in detail.

The first step of the preparation process herein involves the formation a of an aqueous reaction mixture containing particular amounts of a maleate reactant comprising both monovalent cation and calcium salts of maleic acid and a tartrate reactant comprising both monovalent cation and calcium salts of tartaric acid. The total amount of maleate plus tartrate reactants in the reaction mixture will generally range from about 20% to 60% by weight of the mixture, more preferably from about 40% to 55% by weight. Materials which yield these reactants in solution can be dissolved in water to form the reaction mixture used in this process.

Usually both the maleate and tartrate reactants in requisite mixed salt form and amounts can be generated in the reaction mixture in situ. This can be done by combining in aqueous solution certain amounts of maleic acid or maleic anhydride, tartaric acid, a source of calcium cations and, as a neutralizing agent, an hydroxide of a monovalent cation in certain amounts. the molar ratio of maleic acid to tartaric acid in such solutions will generally range from about 0.5:1 to 8:1, more preferably from about 0.9:1 to 1.2:1. The ratio of maleic and tartaric acids which is used will depend upon the relative amounts of tartrate monosuccinate and tartrate disuccinate desired in the builder composition to be prepared.

A souce of calcium cations, which acts as a catalyst for the tartrate succinate-forming reaction, is generally added to such aqueous solutions in an amount such that the ratio of calcium cations to tartaric acid ranges from about 0.1:1 to about 2.0:1, more preferably from about 0.8:1 to 1.5:1. However, within this ratio range, the amount of calcium added should be such that the ratio of moles of calcium cations to total moles of maleic and tartaric acids in solution is less than 1. Any compound which yields calcium cations in solution can be employed as the calcium cation source. Such compounds inlude calcium hydroxide and water-soluble calcium salts. Calcium hydroxide is highly preferred since it acts as both a calcium cation source and a neutralizing agent.

An hydroxide of a monovalent cation is also essentially added to the reactant mixture as a neutralizing agent. This neutralizing agent is usually aded in an amount such that the ratio of moles of monovalent cations to total moles of tartaric acid plus the moles of maleic acid minus the mole of calcium cations ranges from about 2.1:1 to about 3.8:1. More preferably this ratio ranges from about 2.2:1 to about 3:1. The monovalent cation-containing neutralizing agent can be any hydroxide which upon addition to water yields monovalent neutralizing cations in solution. Such neutralizing agents include, for example, alkali metal, ammonium or substituted ammonium hydroxide. Sodium hydroxide is highly preferred.

Enough neutralizing base (e.g. calcium hydroxide and monovalent cation hydroxide) should be added to the reaction mixture to ensure that the reaction mixture is over-neutralized. Thus the reaction mixtures of this invention will generally have a pH within the range of about 8.5 to 13, more preferably from 9.5 to 12.5.

In forming the reaction mixture of the present process, it is possible to employ of the essential reaction mixture components. Precursors of the tartrate and maleate mixed salt reactants in solution can take a variety of forms. For example, tartaric acid in either its D-, L-or DL-stereoisomer form is suitable for use as the precursor of the tartrate reactant. It is also possible to generate tartaric acid in situ by reaction of maleic acid and hydrogen peroxide using, for example, a tungstate catalyst. The maleate reactant can be derived from maleic acid. Maleic acid itself can be formed in aqueous solution by the addition of maleic anhydride to water.

It is, of course, also possible to form the reaction mixture used in the process appropriate by adding the tartrate and maleate reactants in their appropriate salt forms to water and to thereby prepared the reaction mixture without the step of in situ neutralization. If the reaction mixture is formed in this manner, amounts of the tartrate, maleate and calcium materials, as well as added neutralizing agents, should be selected so that the resulting solution corresponds in composition to the hereinbefore described reaction mixtures formed by situ generation of the essential reaction mixture components.

As indicated hereinbefore, the preferred process of the present invention employing reactant molar ratios of maleate to tartrate within the range of 0.9:1 to 1.2:1 is especially advantageous from the reactant converion and reaction kinetis standpoint. A reactant ratios within this range, total reactant conversion levels as high as 84% can be realized in comparison with the much lower conversion percentages reported for preparation of such materials as oxydisuccinate using a maleic anhydride reactant. Without being bound by theory, the improved conversion percentages which can be realized using the preferred process embodiments of the present reaction may be in part due to the inherently greater stability of TMS in the reaction mixture in comparison with oxydisuccinate (ODS) under similar conditions. TMS under conditions used for its formation does not appear to decompose as readily as oxydisuccinate to unreactive by-products such as fumarate, thereby enhancing both TMS formation and subsequent TDS formation from TMS. It should also be noted that irrespective of conversion percentage, production of TMS/TDS mixtures in general can be realized in a relatively short reaction time compared with the extended reaction times which are reported to be required for preaparation of other ether carboxylates such as oxydisuccinate.

It should also be noted that use of the hereinbefore described particular amounts of he calcium cation source is likewise believed to play a role in realizing the improved conversion levels achieved with the process of the present invention. In direct contrast to prior art teaching regarding ether carboxylate preparation (See, for example, U.S. Patent 3,635,830), the amount of calcium in the reaction mixture of the present process should be kept within the hereinbefore described concentration limits in order to avoid formation of a large amount of insoluble or sparingly soluble calcium salts of the maleate and tartrate reactants. Utilization of these reactants in their soluble, mixed salt; e.g. sodium/calcium, form may facilitate the kinetics of the ether carboxylate-forming reaction and accordingly improve product yield.

After the aqueous reaction mixture hereinbefore described has been formed by combining the separate reactants and catalyst, or precursors thereof, in the required concentrations, the TMS/TDS composition forming reaction is carried out by maintaining the aqueous reaction mixture at a temperature of from about 20°C to 120°C, preferably from about 50°C to 80°C, for a period of time sufficient to form a reaction product mixture which contains the desired amounts of the tartrate monosuccinate and tartrate disuccinate compounds of the compositios herein. Reaction times of from about 0.5 to to hours, more preferably from about 1 to 4 hours will generally be suitable for realizing acceptable yields of the compounds used in the builder composition herein.

Since the TMS/ TDS are to be used as detergent builders, it is especially important that such compositions contain especially low levels of alkaline earth metals such as calcium. The builder compositions of this invention should generally contain no more than about 10 mole percent of calcium based on the total moles of TMS and TDS present.

After the ether carboxylate-forming reaction has been completed to the desired extent, the calcium content of the aqueous reaction must be reduced. Removal of calcium to effect this reduction can be carried out in a number of ways known in the art. Frequently, calcium can be removed from the product mixture by adding thereto a calcium precipitating material having a greater affinity for reaction with calcium than do the tartrate monosuccinate and tartrate disuccinate reaction products. Such materials can include, for example, precipitating chelating agents such as ethanehydroxydiphosphonic acid, or salts thereof (EHDP), or calcium precipitating materials such as alkali metal carbonate, pyrophosphate, bicarbonate and/or alkali metal silicate. The resulting calcium precipitate can thereafter be removed from the aqueous reaction product mixture by filtration. An alternate means for removing calcium from the aqueous reaction product mixture involves treatment of the reaction product mixture with an appropriate insoluble ion exchange resin. No matter what technique is employed, calcium content of the aqueous reaction mixture should be reduced to the extent that the ratio of moles of calcium to total moles of tartrate monosuccinate and tartrate disuccinate is less than about 1:10, preferably less than about 1:20.

Preferably, in addition to such calcium reduction processing, the reaction product mixture of the present process may also optionally be treated to remove excess reactants or reaction by-products such as maleates, malates, tartrates and fumarates. This can be accomplished by conventional salt separation procedures using a solvent such as methanol in which these excess reactants and reaction by-products are relatively soluble and in which the desired tartrate monosuccinate and tartrate disuccinate are relatively insoluble.

After the calcium content of the aqueous reaction product mixture has been reduced to the requisite levels, and, if desired, after excess reactants and reaction by-products have been removed, the reaction product mixture may be concentrated by a removal of water to the desired extent. Water removal may, for example, involve substantially complete drying of the reaction product mixture, e.g., by spray drying, so that the TMS/TDS mixture is recovered in solid, e.g., granular, form. Alternatively, the TMS/TDS mixture in the form of an aqueous liquid may be utilized directly in the preparation of builder, detergent compositions or laundry additive products of the types more fully described hereinafter.

After reduction of the calcium content in the reaction product mixture, it is possible, if desired, to acidify the product mixture using conventional acidification or ion exchange techniques to convert the TMS/TDS products therein to their free acid form. Normally, however, the tartrate monosuccinate and tartrate disuccinate materials can be used as builders in their water-soluble salt form, and such acidification is therefore not usually necessary or desirable.

It is also possible, if desired, to separate the individual components of the resulting builder mixture and recover such compounds as substantially pure TMS and TDS materials. Such component separation cab be effected, for example, using conventional liquid chromatographic techniques. For use in some types of detergent compositions, it may be desirable to use either TMS or TDS as substantially pure materials. More frequently, however, recovery of the individual TMS and TDS components as substantially pure materials is neither necessary nor particularly advantageous.

Reaction Sequence I

In this sequence, a mixture of tartrate monosuccinate (TMS) and tartrate disuccinate (TDS) is prepared by a procedure which involves the reaction of maleate salts and tartrate salts. In such a procedure, maleic anhydride (2205g, 22.5 moles) is heated in 2000g of distilled water until dissolved. The resultant solution of maleic acid is cooled to 85 ± 5°C and 2250 g L-(+)-tartaric acid (15.0 moles) is added with stirring at 85 ± 5°C until a homogeneous clear acid solution is obtained.

Separately, 1111g of calcium hydroxide (15.0 moles) is slowly added to a mixture of 4440g of 50% sodium hydroxide solution (55.5 moles) and 1000g distilled water while stirring at a moderate rate such that only a small fraction of unwetted calcium hydroxide is upon the surface of the solution at a time. Stirring is continued until an essentially uniform base mixture is obtained.

The base mixture is then added at a uniform rate over 0.5 hour to the moderately stirred acid solution which is at 70-85°C. The resulting reaction mixture is cooled with warm (ca. 60°C) water in order to maintain a reaction temperature of 90 ± 5°C most of the time. The reaction mixture may, however, boil briefly from time to time. The object is to prevent major losses of water vapor and also to limit the amount of insoluble salt which crystallizes upon the cool reaction vessel walls. As the last 10% of base is added, the reaction temperature is held at 85°C. The reaction mixture is quickly weighed and brought to 13,020g, i.e., 50% active, with 200g of distilled water. (Active is defined here as total weight of organics taken as their sodium salts i.e., sodium maleate and sodium tartrate or 160 x 22.5 moles + 194 x 15.0 moles = 6510g.)

The reaction mixture is immediately heated with steam, stirred moderately in a covered reactor, and a 0.40g sample taken with time arbitrarily set at zero. The reaction mixture, which is a white suspension, is brough to 90-100°C within 10 minutes. Within 15 to 20 minutes of time zero, the reaction mixture clears. Samples (0.40 + 0.04 g) of the reaction solution are taken every half hour to be dissolved in 100 ml 0.1N sulfuric acid solution and immediately submitted for high pressure liquid chromatography (HPLC) analysis in order to monitor the course of the reaction.

The results of HPLC analysis of the 1.5 hour sample indicate that the reaction is to be quenched at the 2.0 hour point. Quenching consists of cooling the reaction product mixture to 50°C within 10 minutes. The homogeneous, almost colorless quenched reaction product solution is reweighed and is made up again to 13,020g with 327g of distilled water to give a reaction product solution containing 50% active.

HPLC analysis indicates that the composition of the organic portion of the reaction product solution is 11.1% tartrate. 1.7% malate, 12.6% maleate, 10.9% fumarate, 35.0% peak 2A, 19.6% peak 2B, 3.3% peak 3A, and 5.9% peak 3B. Peaks 2A and 2B are isomers of sodium tartrate monosuccinate (TMS) and peaks 3A and 3B are isomers of sodium tartrate disuccinate (TDS). Therefore, the HPLC estimated yield of TMS + TDS based upon all peak areas is 63.7%. The approximate weight ratio of TMS:TDS is 86:14. All yields are based upon HPLC refractive index raw data, i.e., are not corrected to mole%. Calculated yield of this reaction based on tartrate is 4.139g.

A second reaction product batch of the same size is made using similar procedures. HPLC analysis indicates that the composition of this second reaction product solution is 9.8% tartrate, 1.7% malate, 12.4% maleate, 10.1% fumarate, 35.0% peak 2A, 18.1% peak 2B, 5.1% peak 3A, and 7.9% peak 3B. Again peaks 2A and 2B are isomers of sodium tartrate monosuccinate (TMS) and peaks 3A and 3B are isomers of sodium tartrate disuccinate (TDS). Therefore, the HPLC-estimated yield of TMS + TDS based upon all peak areas is 66.1%. The approximate weight ratio of TMS:TDS is 80:20. Yield is 4400g based on calculation.

Both reaction product batches are combined to give 26,040g of solution which is calculated to contain 8539g of TMS/TDS and 30 moles of calcium ion. This solution is then diluted with 26,040g of water. While this solution is at 26°C and stirred vigorously, a 28% solution of 7500g (30 mole) of ethanehydroxydiphosphonate disodium salt dissolved in 18,750g of water is added followed by 3178g of 50% sodium hydroxide solution to give a pH of 10.5. Stirring is continued for 18 hours; the final pH is eleven. The resulting precipitate (EHDP-calcium complex) is then removed by filtration using suction filtration equipment with a paper filter, and the filtrate is washed with 4 liters of water. The resulting supernatant, 56 liters, is filtered again through a glass frit to remove any remaining fine particles. This clear solution is then evaporated in a steam heated vat with a compressed air stream blown above the surface to give a solution of 32,550g.

This solution is then poured into 80 liters of vigorously stirred methanol. This is done to help separate the less soluble TMS and TDS from the more soluble maleic and fumaric acid salts. The stirring is continued for 15 minutes followed by a 1/2 hour settling period. Then the liquid is decanted from the gummy solid by siphon. This solid is dissolved in 13,500g of distilled water to give 26,685g of solution which is than poured into 68 liters of methanol, essentially repeating the above. The resulting solid is dissolved in 6 liters of distilled water (pH = 8.4), and the vat is heated with steam. Methanol is removed with a stream of nitrogen directed on the surface of the solution which is well stirred. This is continued until ^{1}H-NMR analysis indicates that the methanol is removed. The resulting solution is 16,380g. To reduce viscosity, 2 liters of water are added, and the mixture is filtered to give 18,887g of solution. This solution is analyzed and found to have the following composition by high pressure liquid chromatography using a refractive index detector: 43.6% TMS/TDS (8,235g or 96.4% recovery by workup), 2.1% tartrate, 0.5% malate, 0.9% maleate, and 1.1% fumarate. The TMS/TDS ratio is 78.2:21.8. The calcium ion level of the solution si 0.048 weight % as determined by atomic absorption.

Reaction Sequence II

A TMS/TDS reaction product mixture is prepared using procedures similar to those set forth in Reaction Sequence I except that the reactants used to form the reaction mixture are maleic anhydride, tartaric acid, sodium hydroxide and calcium hydroxide in a 1.3:1.0:3.93:0.5 molar ratio. The resulting reaction product mixture is determined by high pressure liquid chromatography to contain 17.2% tartrate, 1.5% malate, 9.9% maleate, 10.3% fumarate, TMS (2A 36.2%, 2B 13.4%) and TDS 3A 5.3%, 3B 6.2%). The rest of the sample is a mixture of water and calcium salts.

Calcium is then removed from this mixture by a precipitation procedure using a combination of carbonate salts. In such a procedure 26.5 grams of sodium carbonate and 21.0 grams of sodium bicarbonate (0.25 mole of each salt) are dissolved in 204 grams of water. This solution is then added to 250 grams of the above-described reaction product mixture which contains 0.125 moles of calcium. The resulting mixture is placed in a 1 liter flask equipped with a thermometer and stirrer. This mixture is then heated to 80°C and stirred for 3 hours. After cooling to 25°C while stirring is continued, this mixture is filtered through a sintered glass filter. The resulting filter cake is washed with 20ml of water twice. The filtrate is adjusted to a weight of 1000 grams with the addition of water and then is analyzed. The filtrate is found to contain tartrate - 1.48%; malate - 0.14%; maleate - 1.02%; fumarate - 0.83%; TMS (2A 3.3%, 2B 1.3%); TDS -(3A 0.5%, 3B 0.5%); and calcium - 0.009%. The maleate and fumarate salts are then removed using a methanol precipitation procedure as in Reaction Sequence I.

The following examples illustrate the practice of this invention, but are not intended to be limiting thereof.

EXAMPLE I

A water-softening builder composition is as follows:

Ingredients	Percent (wt.)
TMS/TDS Mixture*	50
2-Dodecenyl Succinate (Na Salt)	50

*Prepared as in Reaction I.

The composition of Example I is added to an aqueous laundry bath at a concentration of 500ppm to reduce water hardness and to enhance the fabric cleaning performance of commercial laundry detergents.

EXAMPLE II

A composition of the type described in Example I is prepared as pre-measured, 50-gram sachets, using water-permeable non-woven cloth as the sachet material. The sachets are simply placed in an aqueous bath to provide water softening and detergency builder activity.

EXAMPLE III

The present development allows the formation of highly built liquid detergents. Previous formulations used high levels of precipitating builders, such as fatty acids or alkylsuccinic acid, but in some conditions these materials may deposit onto fabrics and machine parts. Other soluble builders, such as polycarboyxlate, cannot be incorporated at high levels into liquid detergent formulations.

A heavy-duty, liquid laundry detergent or hard surface cleaner is as follows:

TMS/TDS Mixture	9.2
2-Dodecenyl succinic acid	5.8
Dodecylbenzene sulfonic acid	8.5
C_{10-15} alcohl 7 ethoxylated	9.7
Triethanolamine coconut alcohol sulfate	3.2
Oleic acid	3.2
Triethanolamine	3.5
Sodium hydroxide	2.6
Propanediol	1.7
Ethanol	3.3
Cumene sulfonic acid	5.4
Citric acid	.8
Water	40
DTPMPA*	0.85
Miscellaneous - minors inclusive of enzyme balance to 100	

*Diethylene triamine pentamethylene phosphonic acid.

The above composition has a pH, (1% in water; 20°C,) of 7.8. The liquid composition of the example is homogeneous, and stable on storage at room temperature.

The following examples illustrate additional executions of this invention. The abbreviations used are:

C_{12}HLAS	linear dodecyl benzene sulfonic acid
TEACnAS	triethanolamine alcohol sulfate
$C_{x-y}EO_n$	C_{x-y} alcohol ethoxylated with n moles of ethylene oxide
DTPMPA	diethylene triamine penta(methylene phosphonic acid
S(soil)	(poly(terephthalate propylene glycol ester)
R(elease)	(ethoxylated with about 30 moles of ethylene
P(olymer)	(oxide
DSA	2-decenylsuccinic acid
DDSA	2-dodecenyl succinic acid
TSA	2-tetradecenyl succinic acid
HSA	2-hexadecenyl succinic acid
C_{12-14}FA	coconut fatty acid

TFA triethanolamine
NaCs sodium cumene sulfonate
S(oil) (Tetraethylene penta-amine .15EO.
D(ispersant)

The liquid compositions are prepared by admixing the ingredients, and adjusting pH (1% aqueous solution; 20°C) to the desired level, generally 6.5 to 9.

In the compositions herein, the levels of tartrate succinate typically range from 2-15%, preferably 2-10%, most preferably 3-7%. The level of hydrocarbyl succinate is typically 3-20%, preferably 5-15%. The total of the two components is typically 5-35%, preferably 7-25%. The weight ratios of the tartrated succinate: hydrocarbyl succinate range from 3:1 to 1:6, preferably 2:1 to 1:3.

EXAMPLES

	IV	V	VI	VII	VIII	IX	X	XI	XII
C_{12}HLAS	8.5	11.2	11.2	11.2	11.2	11.2	20	8	15
$C_{13-15}EO_7$	9.7	6.8	6.8	6.8	6.8	6.8	3	14	5
TAECnAS	3.2	3.1	3.1	3.2	3.2	3.1	7	-	10
DDSA	9.2	7.2	7.2	-	-	-	10	-	-
TSA	-	-	-	6.8	-	6	-	-	-
HSA	-	-	-	-	6.2	-	-	5	-
DSA	-	-	-	-	-	-	-	-	8
TMS/TDS	4.5	9.8	5.8	4.5	4.5	9.8	7.5	10	3
Citric acid	0.7	0.7	4.5	0.7	0.3	-	-	1.5	7
Oleic acid	-	3.2	3.2	3.2	1.7	3.2	6	1.5	-
C_{12-14}FA	-	-	-	-	0.9	-	-	-	-
DTPMPA	0.8	0.7	0.7	0.8	0.7	0.7	1	0.5	1
SRP	0.5	0.5	0.5	0.5	0.5	0.5	-	1	0.5
SD	0.3	-	0.3	-	-	-	0.6	-	0.5
Ethanol	3.3	3.2	3.2	3.2	3.2	3.2	-	4	2
Propanediol	1.7	1.6	1.6	1.6	1.8	1.8	-	2	1
TEA	3.5	4.0	4.0	4.0	4.0	4.0	5.0	4.5	4
NaOH	--to neutralize acidic ingredients up to 7.5-7.8 as is --								
NaCS	5.4	4.8	4.8	5.5	6.5	5.4	6.2	2	-
Urea	-	-	-	-	-	-	-	-	7
Polydimethylsiloxane	-	0.2	0.1	0.15	0.1	0.2	0.25	-	0.2
Water and miscellaneous (incl.brightener, enzyme, aesthetics)	-------------balance to 100-------------								

The composition of Example V was tested in a washing machine in a 60°C cycle and compared to VIZIR^R , a liquid detergent containing fatty acid builder. The comparative performance on various types of soil on cotton fabrics are reported below. Product concentration during wash was 1.0%.

The comparative stain removal performance readings represnt the average of the evaluations by two expert judges.

Stain	VIZIR^R	Example V
Tea	Ref.	much better
Blackberry	Ref.	slightly better
Grass	Ref.	slightly better
Spaghetti sauce	Ref.	slightly poorer
Baby food	Ref.	much better
Blood/milk/ink	Ref.	much better
Clay	Ref.	slightly poorer
Blood	Ref.	much better

EXAMPLE XIII

A granular detergent composition comprises the following ingredients:

Ingredient	Percent (Wt)
C_{12} Alkyl Benzene Sulfonate	8.0
C_{12}-C_{13} Alcohol Ethoxylate (EO 6.5)	5.0
Tallow Alcohol Sulfate	3.0
Sodium Perborate (Monohydrate)	19.0
Mixed C_{12}-C_{14} Alkenyl Succinate	15.0
TMS	5.0
Sodium Sulfate	40.0
NaOH/KOH	to crutcher pH 10.2
Enzyme Mix *	0.25
TAED **	1.0
Water and Minors	Balance

*Alcalase/Maxatase 1:1 (dry mix)

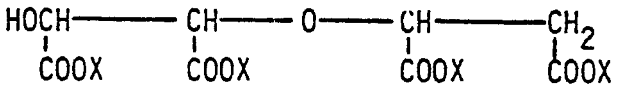
** Tetraacetyl ethylenediamine (dry mix)

An aqueous crutcher mix is prepared and spray-dried. The Enzyme Mix and TAED bleach activator and dry-mixed with the resulting granules.

Claims

1. A detergency builder composition, comprising:
(a) a tartrate succinate component which is a member se lected from the group consisting of:

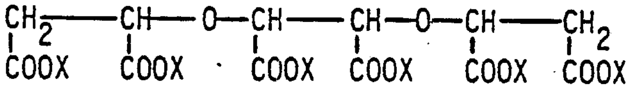
i)



$$\underset{\mathrm{COOX}}{\mathrm{HOCH}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH_2}}$$

wherein X is H or a salt-forming cation;

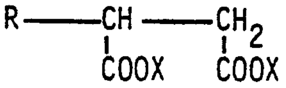
ii)



$$\underset{\mathrm{COOX}}{\mathrm{CH_2}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH_2}}$$

wherein X is H or a salt-forming cation; and iii) mixtures thereof; and

(b) a hydrocarbyl succinate component of the formula:



$$\mathrm{R}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH_2}}$$

wherein R is a hydrocarbyl group and X is H or a salt- forming cation.

2. A composition according to Claim 1 wherein substituent R in the hydrocarbyl succinate component (b) is C_8-C_{18}.

3. A composition according to Claim 2 wherein R in component (b) is C_{12}-C_{16} alkyl or alkenyl.

4. A composition according to Claim 3 wherein component (b) is 2-dodecenyl succinic acid, or water-soluble salt thereof.

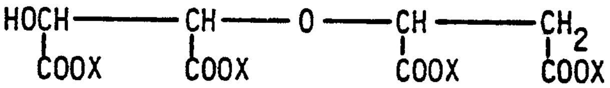
5. A composition according to Claim 3 wherein the weight ratio of component (a):(b) is in the range of 15:1 to 1:15.

6. A composition according to Claim 5 wherein the weight ratio of (a):(b) is 2:1 to 1:3.

7. A detergent composition comprising conventional detersive surfactants and detersive ingredients, and a detergency builder composition which comprises a mixture of:

(a) a tartarte succinate component which is a member selected from the group consisting of:

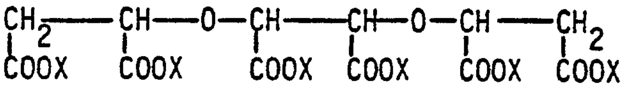
i)



$$\underset{\mathrm{COOX}}{\mathrm{HOCH}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH_2}}$$

wherein X is H or a salt-forming cation;

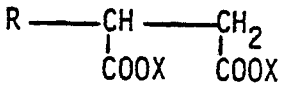
ii)



$$\underset{\mathrm{COOX}}{\mathrm{CH_2}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH_2}}$$

wherein X is H or a salt-forming cation; and iii) mixtures thereof; and

(b) a hydrocarbyl succinate component of the formula:



$$\mathrm{R}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH_2}}$$

wherein R is a hydrocarbyl group and X is H or a salt- forming cation.

8. A detergent composition according to Claim 7 which contains from 1% to 50% by weight of detersive surfactant and from 5% to 45% by weight of the detergency builder composition, the balance comprising conventional detergent ingredients or carriers.

9. A detergent formulation according to Claim 8 wherein the detersive surfactant is a member selected from the group consisting of anionic, cationic, and nonionic detersive surfactants.

10. A detergent composition according to Claim 9 which comprises:

I.A. from 0% to 30% by weight of anionic detersive surfactant selected from conventional detersive alkyl benzene sulfonates, alkyl sulfates, alkyl ether sulfates, soaps, and mixtures thereof;

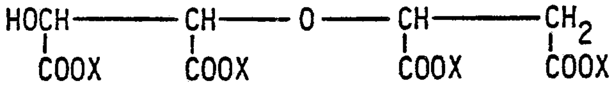
B. from 0% to 30% by weight of a nonionic surfactant selected from conventional detersive ethoxylated alcohols and ethoxylated alkyl phenols, and mixtures thereof; or

C. mixtures of A and B, with the proviso that the composition contains at least 5% by weight of detersive surfactant,

II. at least 10% by weight of a detergency builder component comprising:

(a) a tartrate succinate component which is a member selected from the group consisting of:

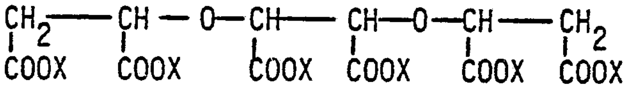
i)



$$\underset{\mathrm{COOX}}{\mathrm{HOCH}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH_2}}$$

wherein each X is H or a salt-forming cation;

ii)

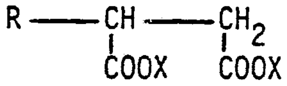


$$\underset{\mathrm{COOX}}{\mathrm{CH_2}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\mathrm{O}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH_2}}$$

wherein each X is H or a salt-forming cation;

iii) mixtures thereof; and

(b) a hydrocarbyl succinate component of the formula:



$$\mathrm{R}-\underset{\mathrm{COOX}}{\mathrm{CH}}-\underset{\mathrm{COOX}}{\mathrm{CH_2}}$$

wherein R is a hydrocarbyl group and X is H or a salt forming cation, the weight ratio of (a):(b) being in the range of 2:1 to 1:3; and

III. the balance of the composition comprising conventional detergent ingredients.

11. A composition according to Claim 10 wherein the hydrocarbyl succinate component of the builder is a C_{12}-C_{16} alkyl or alkenyl succinate.

12. A composition according to Claim 11 wherein the alkenyl succinate is 2-dodecenyl succinic acid, or water-soluble salt thereof.

13. A composition according to any of Claims 7-12 which is formulated as a liquid laundry detergent, or is fomulated releasably on a sheet or other carrier substrate, or releasably contained in pouches, or is formulated as a bar, powder, granule, tablet or flowable gel.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 20 1564

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE-A-2 057 258 (UNILEVER N.V.) * page 17, table 4, claims 1,5-7 * ---	1,9,10	C 11 D 3/20 C 11 D 3/00
A	US-A-4 107 064 (G.E. NELSON et al.) * claims 1,9, example 1 * ---	1,9,10	
A	DE-A-2 656 251 (COLGATE-PALMOLIVE CO.) * claims 1,6 * ---	1,9,10	
D,A	GB-A-1 528 171 (DIAMOND SHAMROCK EUROPE LTD.) * claims 1,5 * -----	1,9,10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 11 D 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	24-11-1987	SCHULTZE D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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& : member of the same patent family, corresponding document