

[54] **DETERGENT COMPOSITIONS**

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[58] **Field of Search**..... **252/89, 544; 260/475 R**

[56]

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Primary Examiner—William E. Schulz

[57]

ABSTRACT

Certain partial esters and partial amides of cyclic poly-carboxylic acids can act as detergency builders and fabric softeners when incorporated into otherwise conventional fabric washing detergent compositions.

3 Claims, No Drawings

DETERGENT COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to detergent compositions adapted for use in fabric washing and which contain chemical compounds which act as detergency builders and fabric softeners. The invention also relates to novel chemical compounds for use in such detergent compositions.

2. Description of Prior Art

Detergent compositions adapted for use in fabric washing, particularly when such washing is to be conducted in domestic fabric washing machines, generally comprise as major ingredients detergent-active compounds and detergency builders. The most commonly used detergency builders are the condensed phosphates, particularly sodium tripolyphosphate, but the use of other inorganic and organic materials, such as sodium nitrilotriacetate and sodium ethane-1-hydroxy-1,1-diphosphonate, has been proposed.

It has been suggested that the use of condensed phosphates in detergent compositions contributes to eutrophication. Considerable effort has been expended to find alternative materials not containing phosphorus which can effectively build the detergency of a detergent composition whilst not being too expensive or having any other deleterious properties.

Another important feature of a fabric washing detergent composition is its ability to impart a soft feel to fabric articles. The majority of conventional fabric washing detergent compositions do not alleviate the harshening of fabric articles caused by repeated washes which, in the case of articles of clothing, may make the fabric articles less comfortable to have in contact with the human skin.

Various washing compounds have been proposed as additives in fabric washing detergent compositions to alleviate this harshening. In general the incorporation of large amounts of softening additives in detergent compositions is undesirable, as such additives usually do not have any other useful function and take up space in the detergent composition formulation, which space might otherwise be utilised for some other multi-functional ingredient. Moreover, the degree of fabric softening achieved by such additives to the detergent compositions is usually very slight. Alternative proposals have involved the use of separate additives for use during the rinsing operation, which separate additives are intended to improve the feel of the fabric articles. More effective softening is achieved by the use of rinse additives, but this necessitates a separate action on the part of the housewife, and the use of a second product during the washing process, and is often considered to be undesirable.

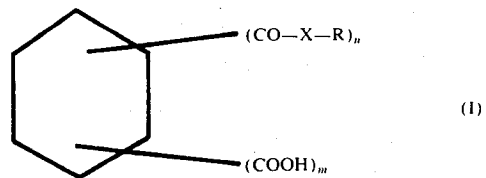
Accordingly, the use in a fabric washing detergent composition of a single compound which acts both as an effective detergency builder and as an effective fabric softener would result in an improved detergent composition.

SUMMARY OF THE INVENTION

By the present invention it has been found that certain partial esters and partial amides of cyclic polycarboxylic acids can act as detergency builders and fabric softeners when incorporated into otherwise conventional fabric washing detergent compositions. These

partial esters and partial amides of cyclic polycarboxylic acids are hereinafter referred to as "polycarboxylic acid derivatives".

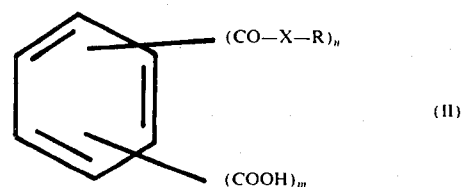
According to the invention, a detergent composition comprises at least one detergent-active compound and at least one polycarboxylic acid derivative, or a water-soluble or water-dispersible salt thereof, having the general formula:



wherein X is O or NH, R is a substantially linear primary or secondary alkyl or substantially linear primary or secondary alkenyl chain containing on average from 14 to 20, preferably 16 to 18, carbon atoms, n is 1 to 4, preferably 1 or 2, m is 2 to 5, preferably 2 or 3, and the cyclic ring may be fully or partially saturated, or fully aromatic, ($n + m$) not being greater than 6.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a preferred embodiment of the invention, the cyclic ring of the polycarboxylic acid derivative is fully aromatic, and the polycarboxylic acid derivative accordingly has the general formula:



wherein X, R, n and m have the same significance as in formula I.

It will be apparent from this disclosure to those skilled in the art that, although the polycarboxylic acid derivatives of the invention will function most effectively as detergency builders and fabric softeners when the groups R in the above formulae are linear, nevertheless a minor proportion of slightly branched R groups may be present without a significant drop in performance being incurred.

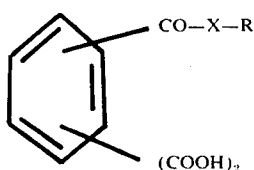
Polycarboxylic acid derivatives of the invention may be incorporated in a detergent composition either in the form of a partial free acid or as a water-soluble or water-dispersible salt thereof. Alkali-metal, particularly sodium and potassium, salts are preferred, but other salts such as ammonium or substituted ammonium, e.g. trimethylammonium and triethylammonium, may be used if desired.

The polycarboxylic acid derivatives of the invention will normally comprise from about 5 to about 60% by weight of a detergent composition, preferably from about 15 to about 50% by weight.

Particularly preferred polycarboxylic acid derivatives of the invention are:

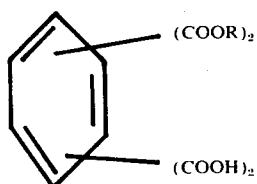
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a. Compounds of general formula:



wherein X is O or NH and R is a substantially linear primary or secondary alkyl chain containing on average from 16 to 18 carbon atoms; and

b. Compounds of general formula:



wherein R is a substantially linear primary or secondary alkyl chain containing on average from 16 to 18 carbon atoms.

In general, the aromatic polycarboxylic acid partial esters may be prepared by reacting appropriate molar amounts of an aromatic polycarboxylic acid, or an anhydride thereof, with a long-chain aliphatic alcohol. In some instances transesterification may be required. The techniques associated with esterification and transesterification are familiar to those skilled in the synthesis of organic chemical compounds. The Examples given below illustrate in detail typical methods suitable for the preparation of the aromatic polycarboxylic acid derivatives of the invention.

Generally speaking, the nature of the detergent-active compound or compounds in a detergent composition of the invention is not a critical feature and any of the detergent-active compounds conventionally used in fabric washing detergent compositions may be utilized. Those skilled in the art of formulating detergent compositions will be familiar with these detergent-active compounds and the various amounts and combinations in which they may advantageously be used. The detergent-active compound or compounds may be anionic, nonionic, amphoteric or zwitterionic in character.

The detergent-active compound content of the detergent composition of the invention will be from about 1 to about 50%, preferably from about 2 to 35%, and particularly preferably from about 5 to about 25%, by weight of the detergent composition.

Typical anionic detergent-active compounds are water-soluble or water-dispersible salts of various organic acids. The cations of such salts are generally alkali-metals, such as sodium and, less preferably, potassium, but other cations, such as ammonium and substituted ammonium, can be used if desired. Examples of suitable organic acids are: alkyl benzene sulphonic acids, the alkyl chains of which contain from about 8 to about 20 carbon atoms, such as p-dodecyl benzene sulphonic acid and linear alkyl ($\text{C}_{10}\text{-C}_{15}$) benzene sulphonic acid; the mixtures of sulphonic acids obtained

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by reacting linear and branched olefins, particularly linear "cracked-wax" or "Ziegler" alpha-olefins, containing from about 8 to about 22 carbon atoms, with sulphur trioxide; alkyl sulphonic acids obtained by reacting alkanes containing from about 8 to about 22 carbon atoms with sulphur dioxide/oxygen or sulphur dioxide/chlorine (followed by hydrolysis in the latter case), or by the addition of bisulphite to olefins, particularly linear "cracked-wax" or "Ziegler" alpha-olefins, containing from about 8 to about 22 carbon atoms; alkyl sulphuric acids obtained by reacting aliphatic alcohols containing from about 8 to about 22 carbon atoms with sulphur trioxide; alkyl ether sulphuric acids, obtained by reacting molar quantities of aliphatic alcohols containing from about 6 to about 18 carbon atoms with from about 1 to about 15 moles of ethylene oxide, or a suitable mixture of ethylene oxide and propylene oxide, and subsequently reacting the alkoxyated alcohol with sulphur trioxide to yield the required acid; and natural or synthetic aliphatic carboxylic acids, particularly those derived from natural sources such as tallows, coconut oil, palm oil, palm kernel oil and groundnut oil.

Examples of suitable nonionic detergent-active compounds are: condensates of alkyl-phenols having an alkyl group (derived, for example, from polymerised propylene, diisobutylene, octene, dodecene or nonene) containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with about 5 to 25 moles of ethylene oxide per mole of alkyl-phenol; condensates containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide with the reaction product of ethylenediamine and excess propylene oxide; condensates of linear or branched-chain aliphatic alcohols containing from 8 to 18 carbon atoms with ethylene oxide, e.g. a coconut alcohol-ethylene oxide condensate containing about 6 to 30 moles of ethylene oxide per mole of coconut alcohol; long-chain tertiary amine oxides corresponding to the general formula $\text{R}_1\text{R}_2\text{R}_3\text{N} \rightarrow \text{O}$, wherein R_1 is an alkyl radical containing from about 8 to 18 carbon atoms and R_2 and R_3 are each methyl, ethyl or hydroxy ethyl radicals, such as dimethyldodecylamine oxide, dimethyloctylamine oxide, dimethylhexadecylamine oxide and N-bis (hydroxyethyl) dodecylamine oxide; long-chain tertiary phosphine oxides corresponding to the general formula $\text{RR}'\text{R}''\text{P} \rightarrow \text{O}$, wherein R is an alkyl, alkenyl or monohydroxyalkyl radical containing from 10 to 18 carbon atoms and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms, such as dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, diethyldodecylphosphine oxide, bis (hydroxymethyl) dodecylphosphine oxide, bis (2-hydroxyethyl) dodecylphosphine oxide, 2-hydroxypropylmethyltetradecylphosphine oxide, dimethylolelylphosphine oxide and dimethyl-2-hydroxydodecylphosphine oxide; and dialkyl sulphoxides corresponding to the general formula $\text{RR}'\text{S} \rightarrow \text{O}$, wherein R is an alkyl, alkenyl, beta- or gamma-monohydroxyalkyl radical or an alkyl or beta- or gamma-monohydroxyalkyl radical containing one or two other oxygen atoms in the chain, the R groups containing from 10 to 18 carbon atoms and wherein R' is a methyl, ethyl or alkylol radical, such as dodecyl methyl sulphoxide, tetradecyl methyl sulphoxide, 3-hydroxytridecyl methyl sulphoxide, 2-

hydroxydodecyl methyl sulphoxide, 3-hydroxy-4-dodecyloxybutyl methyl sulphoxide, 2-hydroxy-3-decyloxypropyl methyl sulphoxide, dodecyl ethyl sulphoxide, 2-hydroxydodecyl ethyl sulphoxide and dodecyl-2-hydroxyethyl sulphoxide.

Examples of suitable amphoteric detergent-active compounds are: derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilising group, such as sodium-3-dodecylaminopropionate, sodium-3-dodecylaminopropanesulphonate and sodium N-2-hydroxydodecyl-N-methyl-taurate.

Examples of suitable zwitterionic detergent-active compounds are: derivatives of aliphatic quaternary ammonium compounds, sulphonium compounds and phosphonium compounds in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilising group, such as 3-(N,N-dimethyl-N-hexadecylammonium) propane-1-sulphonate betaine, 3-(N,N-dimethyl-N-hexadecyl-ammonium)-2-hydroxypropane-1-sulphonate betaine, 3-(dodecylmethyl-sulphonium) propane-1-sulphonate betaine, and 3-(cetyl-methylphosphonium) ethane sulphonate betaine.

Further examples of suitable detergent-active compounds commonly used in the art are given in "Surface Active Agents, Volume I" by Schwartz and Perry (Interscience 1949) and "Surface Active Agents, Volume II" by Schwartz, Perry and Berch (Interscience 1958).

A polycarboxylic acid derivative of the invention may be utilised as the sole detergency builder in a detergent composition, or if desired may be used in combination with one or more known detergency builders. In particular, polycarboxylic acid derivative may be used as a partial replacement for sodium tripolyphosphate in an otherwise conventional sodium tripolyphosphate-containing detergent composition.

When a polycarboxylic acid derivative of the invention is used in a detergent composition in combination with other detergency builders, the amount of such other detergency builders will not be more than about 20%, and preferably not more than 15%, by weight of the detergent composition.

Many detergency builders are known, and those skilled in the art of formulating fabric-washing detergent compositions will be familiar with these materials. Examples of known detergency builders are sodium tripolyphosphate; sodium orthophosphate; sodium pyrophosphate; sodium trimetaphosphate; sodium ethane-1-hydroxy-1, 1-diphosphonate; sodium carbonate; sodium silicate; sodium citrate; sodium oxydiacetate; sodium carboxymethyloxysuccinate; sodium nitrilotriacetate; sodium ethylene-diaminetetraacetate; sodium salts of long-chain dicarboxylic acids, for instance straight chain (C₁₀ to C₂₀) alkyl or alkenyl succinic acids and malonic acids; sodium salts of alpha-sul-

phonated long-chain monocarboxylic acids; sodium salts of polycarboxylic acids; i.e. acids derived from the polymerisation or copolymerisation of unsaturated carboxylic acids and unsaturated carboxy acid anhydrides such as maleic acid, acrylic acid, itaconic acid, methacrylic acid, crotonic acid and acetic acid, and the anhydrides of certain of these acids, and also from the copolymerisation of the above acids and anhydrides with minor amounts of other monomers, such as ethylene, vinyl methyl ether, vinyl chloride, vinyl acetate, methyl methacrylate, methyl acrylate and styrene; and modified starches such as starches oxidised, for example using sodium hypochlorite, in which some anhydroglucose units have been opened to give dicarboxylic units.

Furthermore, a detergent composition of the invention may contain any of the conventional fabric-washing detergent composition ingredients in any of the amounts in which such conventional ingredients are usually employed therein. Examples of these additional ingredients are lather boosters, such as coconut monoethanolamide and palm kernel monoethanolamide; lather controllers; inorganic salts such as sodium sulphate and magnesium sulphate; oxygen-releasing bleaching agents such as sodium perborate, sodium percarbonate, and peracid bleach precursors such as tetraacetyl ethylene diamine; chlorine-releasing bleaching agents such as trichloroisocyanuric acid and sodium and potassium dichloroisocyanurates; antiredeposition agents, such as sodium carboxymethylcellulose; and, usually present only in minor amounts, perfumes, colourants, fluorescenters, corrosion inhibitors, germicides and enzymes.

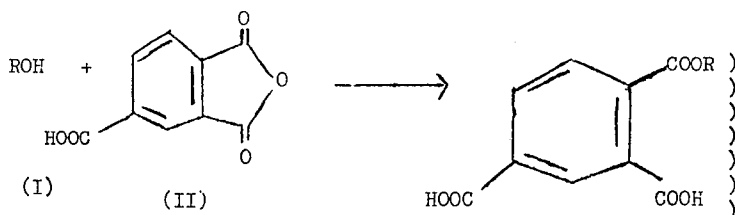
A detergent composition of the invention can be prepared using any of the conventional manufacturing techniques commonly used or proposed for the preparation of detergent compositions, such as slurry-making followed by spray-drying or spray-cooling, and subsequent dry-dosing of sensitive ingredients not suitable for incorporation prior to the drying step. Other conventional techniques, such as noodling, granulation, and mixing by fluidisation in a fluidised bed, may be utilised as and when necessary. Such techniques are familiar to those skilled in the art of detergent composition manufacture.

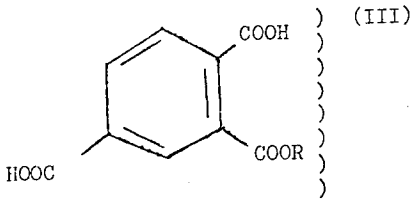
By using such conventional manufacturing techniques, a detergent composition of the invention may be prepared in any of the common physical forms associated with detergent compositions, such as powders, flakes, granules, noodles, cakes, bars and, in some cases, liquids.

The following Examples, in which all parts and percentages are by weight, illustrate the preparation of certain aromatic polycarboxylic acid derivatives of the invention, and their utility in detergent compositions.

EXAMPLE I

Preparation of a tallow monoester of trimellitic acid:



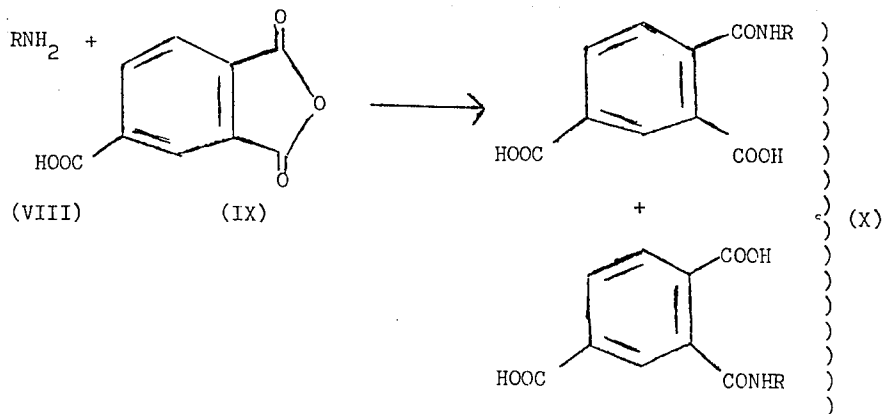
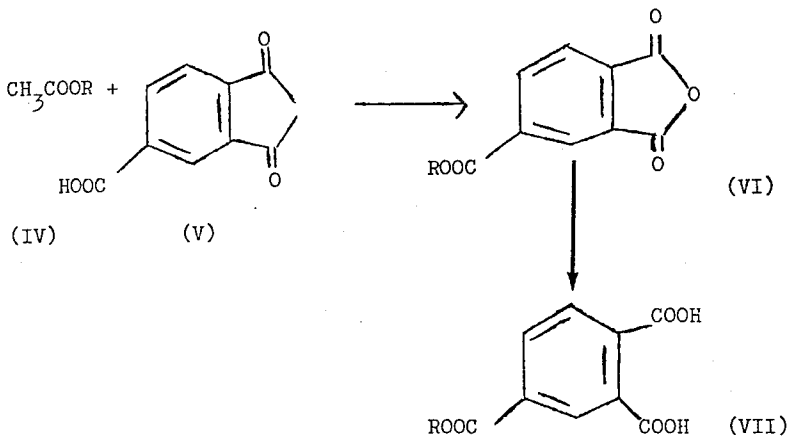


wherein R is a "tallow" group, i.e. a predominantly saturated linear hydrocarbon chain containing an average 18 carbon atoms.

Equimolar quantities of tallow alcohol (I) and trimellitic anhydride (II) were heated together until the temperature reached about 150°C. At this temperature the volume of the reaction mixture began to expand rapidly, and the reaction was controlled by removing the source of heat. On cooling the reaction mixture solidified and was recrystallised from aqueous acetone. Analysis revealed that the product mixture (III) had been produced.

EXAMPLE II

Preparation of a further tallow monester of trimellitic acid:



wherein R is a "tallow" group as in Example I.

This was prepared by transesterification. An equimolar mixture of tallow acetate (IV) and trimellitic anhydride (V) were heated under reflux up to 310°C for 4 hours, with removal of acetic acid in a Dean and Stark apparatus. The product (VI) was poured into petroleum ether at 80°C, boiled, allowed to crystallise at 0°C, and filtered. The anhydride ring was opened with aqueous sodium hydroxide to give compound (VII) in the form of its disodium salt. Its structure was confirmed by elemental and spectroscopic analysis.

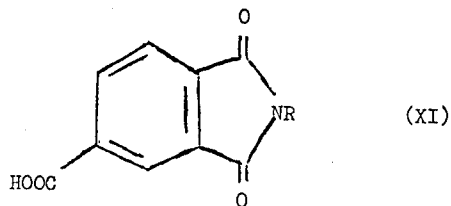
EXAMPLE III

Preparation of a C₁₈ alkyl amide of trimellitic acid:

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wherein R is a substantially linear alkyl group containing an average 18 carbon atoms.

Equimolar quantities of octadecyl amine (VIII) and trimellitic anhydride (IX) were mixed and dissolved in dimethylformamide at 25°C. A clear solution formed and was allowed to stand for 1 hour. A five-fold excess of water was added and the product (X) precipitated. Analysis confirmed its structure, but also showed that about 20–30% of the product was in the form of an imide (XI).



EXAMPLE IV

Preparation of a tallow diester of pyromellitic acid:

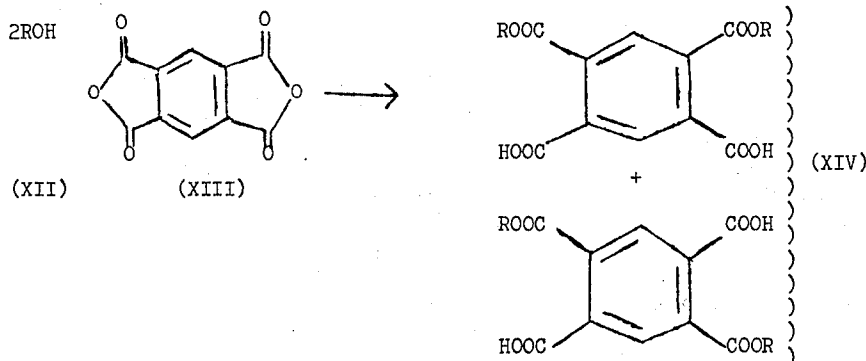
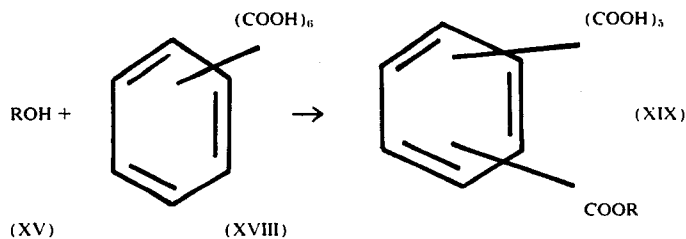
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where R is a substantially linear alkyl group containing on an average 18 carbon atoms, ROH being a commercially available C₁₈ alcohol (trade name: "Alfol").

The alcohol (XV; 1 mole) and the hemimellitic acid (XVI; 4 moles) were refluxed in toluene in the presence of concentrated sulphuric acid, water formed during the reaction being collected in a Dean and Stark apparatus. The mole ratio of alcohol: acid was chosen to give a maximum probability of forming the desired mono-ester; a higher proportion of alcohol would have favoured an increased yield of di-esters, etc. The refluxing was continued until no further moisture was collected in the Dean and Stark apparatus. The toluene was removed using a rotary evaporator, and the ester, and residual unreacted alcohol, were separated from the unreacted acid by methanol extraction using a Soxhlet extractor. The ester (XVII) was crystallised from the methanol.

EXAMPLE VI

Preparation of a C₁₈ alkyl monoester of mellitic acid:

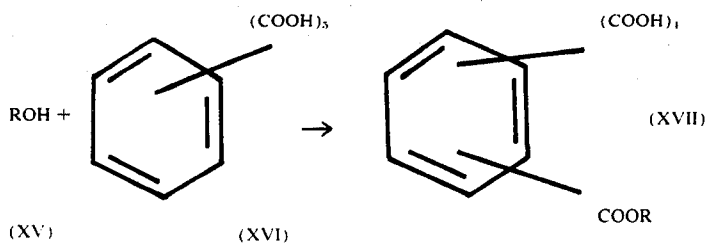


where R is a "tallow" group.

Tallow alcohol (XII; 2 moles) and pyromellitic anhydride (XIII; 1 mole) were heated together at 160°C for 1 hour. The reaction mixture solidified on cooling, and was recrystallised from aqueous acetone. Analysis revealed the product (XIV).

EXAMPLE V

Preparation of a C₁₈ alkyl monoester of hemimellitic acid:



where R is the same as in Example V.

This was prepared by a procedure exactly analogous to that used in Example V, a 1:4 molar ratio of alcohol (XV) to mellitic acid (XVIII) again being used to give a high yield of the monoester (XIX).

EXAMPLES VII TO X

Four detergent compositions according to the invention (Examples VII to X) and a comparative composition A were prepared having the following formulations:

| Component Ex: | Parts | | | | |
|---|-------|------|-----|-----|-----|
| | VII | VIII | IX | X | A |
| Sodium C ₁₁₋₁₃ alkyl benzene sulphonate | 5 | 5 | 5 | 5 | 5 |
| Sodium sulphonate (Na ₂ O:SiO ratio 1:2) | 8 | 8 | 8 | 8 | 8 |
| Sodium sulphate | 6 | 6 | 6 | 6 | 6 |
| Sodium carboxymethyl cellulose | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Sodium perborate | 20 | 20 | 20 | 20 | 20 |
| Fluorescer (Photine CBU) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Sodium tripolyphosphate | — | — | 10 | 10 | 40 |

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Examples IX and X had detergencies comparable to that of the control, and again showed superior softening properties.

EXAMPLES XI TO XVIII

The following compositions according to the invention also possess good detergencies and show superior wash softening characteristics when compared with conventional fabric-washing detergent compositions built wholly with sodium tripolyphosphate.

| Component Ex: | Parts | | | | | | | |
|---|-------|-----|------|-----|-----|-----|------|-------|
| | XI | XII | XIII | XIV | XV | XVI | XVII | XVIII |
| Sodium C ₁₁₋₁₃ alkyl benzene sulphonate | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Sodium alkaline silicate (Na ₂ O:SiO ₂ ratio 1:2) | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| Sodium sulphate | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| Fluorescer (Photine CBU) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Sodium carboxymethyl-cellulose | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Sodium perborate | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Sodium tripolyphosphate | — | — | — | 10 | 10 | 10 | 10 | 10 |
| Tallow trimellitate (Ex II) * | 40 | — | — | — | 30 | — | — | — |
| C ₁₈ alkyl amide trimellitate (Ex III) * | — | 40 | — | — | — | 30 | — | — |
| C ₁₈ alkyl hemimellitate (Ex V) * | — | — | 40 | — | — | — | 30 | — |
| C ₁₈ alkyl mellitate (Ex VI) * | — | — | — | 40 | — | — | — | 30 |

* In the form of sodium salts.

| | | | | | |
|---------------------------------|----|----|----|----|---|
| Ditallow pyromellitate (Ex: 4)* | 40 | — | 30 | — | — |
| Tallow trimellitate (Ex: 1)* | — | 40 | — | 30 | — |

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*In the form of sodium salts.

Each composition was used to wash artificially soiled cotton test cloths in a Terg-O-Tometer apparatus, using 30°H hard water (Ca:Mg ratio 2:1) at 95°C for 30 minutes at a product concentration of 0.6%, followed by a cold rinse. After drying the test cloths were ranked for softness by a panel, and were used in a photometric determination of the detergency produced by each composition. The following results were obtained:

| Detergency results: | | | | | |
|---------------------|------|------|------|------|------|
| Example: | VII | VIII | IX | X | A |
| Detergency: | 49.5 | 55.9 | 60.0 | 62.2 | 63.6 |

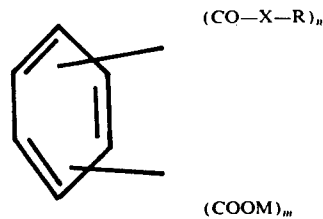
Softness ranking

Example: VII and VIII were softer than IX and X which were very much softer than A.

From these results it can be seen that the compositions of Examples VII and VIII, although not being as effective at cleaning as the control, nevertheless exhibited reasonable detergency results and produced considerably greater wash softening than the control.

What is claimed is:

1. A detergent composition comprising
 - a. from 1-50% by weight of an anionic, a nonionic, an amphoteric, a zwitterionic organic detergent active compound or a mixture thereof, and
 - b. from 5-60% by weight of a polycarboxylic acid derivative of the following general formula



50 wherein X = O or NH

R = a substantially linear primary or secondary alkyl or alkenyl chain with 14-20 carbon atoms

n = 1-4

m = 2-5

55 n + m = ≤ 6

M = H, Na, K, NH₄, trimethyl- or triethylammonium.

2. A composition according to claim 1, wherein n = 1, R is a substantially linear primary or secondary alkyl chain with 16-18 carbon atoms, and m = 2.

3. A composition according to claim 1, wherein X = O, n = 2, m = 2 and R is a substantially linear primary or secondary alkyl chain with 16-18 carbon atoms.

* * * * *