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DETERGENT COMPOSITION

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ABSTRACT OF THE DISCLOSURE

Detergent compositions are provided affording reduced tendency to chemically burn users which consist essentially of a synthetic organic detergent and a small, effective amount of traumatic acid or salt thereof.

REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my copending application Ser. No. 380,071 filed July 2, 1964, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

Synthetic organic detergents have found widespread use for cleaning dishes, clothes and household surfaces. Typically these materials are purveyed as equeous or aqueous-alcoholic solutions, e.g. typically light duty liquid detergent, suitable for dishes, comprising an aqueous alkyl benzene sulfonate solution. For some persons, use of these products produces a roughness or reddening of the hands. This "dishpan hands" effect is actually a chemical burn of the skin tissue.

Prior art

It has been proposed to avoid these burns by interposition of barriers such as gloves and pre-use hand creams. These expedients interfere with ordinary dexterity and digital control and are relatively costly. Use of lotions to soothe the skin following detergent exposure has also been resorted to.

SUMMARY OF THE INVENTION

It is a major objective of the present invention to provide a novel detergent composition which contains a chemical burn palliative. It is a further object to provide a detergent product comprising synthetic organic detergent having a tendency to chemically burn skin tissue and an effective amount of burn medication therein.

Accordingly, it has now been discovered that a detergent composition producing lessened chemical burn maleeffects consists essentially of the synthetic organic detergent and a small amount of traumatic acid or salt thereof, effective to counteract skin irritating properties of the detergent. The detergent may be solid, as in the case of bar soap; granular, as in powder detergents or soaps; or liquid, as in aqueous and or alcoholic solutions of alkyl aryl sulfonates. Suitable alcohols include lower alkanols having up to 3 carbon atoms.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Traumatic acid is also known as 1-decene-1, 10-dicarboxylic acid and exists in cis and trans forms, the latter, hereinafter referred to as TTA, being the more biologically active.

TTA may be prepared as follows: Undecylenic acid is oxidized to hydroxyformoxyhendecanoic acid with hydrogen peroxide in formic acid which is then hydrolyzed

to 10,11-dihydroxyhendecanoic acid with sodium hydroxide. Treatment with periodic acid transforms the 10, 11-dihydroxyhendecanoic acid into the sebacic semi-aldehyde which is condensed with malonic acid in the presence of pyridine. Upon acidification of the condensation mixture, 1-decene-1,10-dicarboxylic acid, i.e. traumatic acid, precipitates. This product is purified by recrystallization from a solvent.

Salts of TTA may be prepared by replacement of the carboxyl hydrogen with the selected metal from a suitable metal salt, e.g. carbonate, acetate, chloride and the like containing the metal ion of interest, e.g. cobalt carbonate.

Quantities of traumatic acid or salt employed are typically quite small. Thus as little as 0.00005 percent by weight in a detergent composition will prove effective in most case. Seldom will more than 1 to 2 percent be required or desired.

In addition to the traumatic acid or salt, the present detergent composition may contain in conventional, effective amounts builder salts, perfumes, optical brighteners, opacifiers, binders and like additives for specific purposes.

The preferred form of traumatic acid is the transisomer and particularly salts thereof with metals having an atomic number between 11 and 30 and in Groups I–A, I–B, VII–B, VIII and II–B of the Periodic Chart of the Elements (Merck Index, 6th edition) with the proviso that the Group VIII metal have an odd atomic number, i.e. metals selected from sodium, potassium, manganese, cobalt, copper and zinc.

The term "synthetic organic detergent" herein includes both soaps, i.e. the product of the saponification of natural fats or oils, or their constituent long chain fatty acids, with alkali metal hydroxide such as sodium hydroxide, and those surface active agents commonly so called.

With respect to the synthetic organic detergent, useful materials are the cationic, nonionic, amphoteric or anionic detergents.

Suitable synthetic detergents thus include cationic detergents such as the amines, particularly primary fatty amines such as lauric amine, myristic amine, palmitic amine, stearic amine, oleyl amine, linoleyl amine, coco amine and tallow amine. Also N-fatty propylene diamine and heterocyclic tertiary amines as well as fatty halides, e.g. stearyl dimethyl benzyl ammonium chloride, dodecylbenzene chloride, lauryl pyridinium chloride and sulfates, e.g. lauryl pyridinium bisulfate can be used.

In general, suitable non-ionic detergents include water-soluble non-ionic polyalkylene oxide detergents such as are produced by the introduction of alkylene oxide group into an organic hydrophobic compound or group having an aliphatic or aromatic structure. The hydrophobic organic group generally contains at least 8 carbon atoms and up to about 30 carbon atoms. Condensed with the hydrophobic group are at least 5 and preferably up to about 50 alkylene oxide groups. It is preferred to use the polyoxyethylene condensates derived from ethylene oxide. Among the non-ionic detergents, it is preferred to use the polyalkylene oxide condensates of alkyl phenol, such as the polyoxyethylene ethers of alkyl phenols having an alkyl group of at least about six, and usually about 8 to 12 carbons, and an ethylene oxide ratio (No. of moles (per phenol) of about 7.5, 8.5, 11.5 and 20, though the number of ethylene oxide groups will be usually from about 8 to 18. The alkyl substituent on the aromatic nucleus may be di-isobutylene, diamyl, polymerized propylene, dimerized C_6–C_7 olefin, and the like.

Further suitable detergents are the polyoxyalkylene esters of organic acids, such as the higher fatty acids,

rosin acids, tall oil acids, or acids from the oxidation of petroleum, et cetera. These polyglycol esters will contain usually from about 12 to about 30 moles of ethylene oxide or its equivalent and about 8 to 22 carbons of the acyl group. Suitable products are refined tall oil condensed with 16 or 20 ethylene oxide groups, or similar polyglycol esters of lauric, stearic, oleic acids, etc.

Additional non-ionic agents are the polyalkylene oxide condensates with higher fatty acid amides, such as the higher fatty acid primary amides, mono- and di-ethanolamides. Suitable agents are coconut fatty acid amide condensed with about 10 to 50 moles of ethylene oxide. The fatty acyl group will have similarly about 8 to 22 carbons, and usually about 10 to 18 carbon atoms, in such products. The corresponding sulfonamides may be used also if desired.

Other suitable polyether non-ionic detergents are the polyalkylene oxide ethers of higher aliphatic alcohols. Suitable fatty alcohols having a hydrophobic character, preferably 8 to 22 carbons, are lauryl, myristyl, cetyl, stearyl and oleyl alcohols which may be condensed with an appropriate amount of ethylene oxide, such as at least about 6, and preferably about 10 to 30 moles. A typical product is oleyl alcohol condensed with about 12, 15 or 20 moles of ethylene oxide. The corresponding higher alkyl mercaptans or thioalcohols condensed with ethylene oxide are suitable in the present invention also. The water-soluble polyoxyethylene condensates with hydrophobic polyoxypropylene glycols may be employed also.

Further suitable non-ionic detersive materials are the higher fatty acid alkanolamides, such as the monoethanolamides, diethanolamides and isopropanolamides wherein the acyl radical has about 10 to 14 carbon atoms and amine oxides. Examples are coconut (or equivalent lauric), capric and myristic diethanolamide, monoethanolamide and isopropanolamide, dodecyl dimethyl amine oxide and dimethyl acetoxyalkylamine oxide where alkyl is C_{11}–C_{14}.

Other suitable synthetic detergents are the anionic aromatic detergents, e.g. water-soluble higher alkyl aryl sulfonate detergents particularly those having from 8 to about 18 carbon atoms in the alkyl group. It is preferred to use the higher alkyl benzene sulfonate detergent for optimum effects, though other similar detergents having a mononuclear aryl nucleus, such as toluene, xylene, or phenol, may be used also. The higher alkyl substituent on the aromatic nucleus may be branched or straight-chained in structure, examples of such group being nonyl, dedecyl and pentadecyl groups derived from polymers of lower mono-olefins, decyl, keryl, and the like.

Illustrative of suitable aliphatic anionic detergents are the normal and secondary higher alkyl sulfate detergents, particularly those having about 8 to 18 carbons in the fatty alcohol residue, such as lauryl (or coconut fatty alcohol) sulfate and tallow alcohol sulfate. Other suitable detergents are the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g. oleic acid ester of isothionic acid; the higher fatty acid (e.g. coconut) ethanolamide sulfate; the higher fatty acid amide of amino alkyl sulfonic acids, e.g. lauric acid amide of taurine; and the like.

These sulfate and sulfonate detergents are used in the form of their water-soluble salts, such as the alkali metal and nitrogen-containing, e.g. lower alkylolamine, salts. Examples are the sodium, potassium, ammonium, isopropanolamine, mono- and tri-ethanolamine salts of said higher alkyl benzene sulfonate, higher alkyl sulfate and the like. In commercial practice, it is preferred to use the alkali metal salts.

Typical specific examples are: the sodium salt of a sulfate ester of an alkylphenoxypoly (ethyleneoxy) ethanol, the ammonium salt of this sulfate ester, sodium methyl oleyl taurate, sodium alkyl naphthalene sulfonate, alkyl acyl sodium sulfonate, sodium tetrahydronaphthalene sulfonate, sodium alkyl aryl sulfonate, alkyl amido sulfate, cocomonoglyceride sulfate, dodecylbenzene sodium sulfonate, dodecylbenzene sulfonic acid, tridecylbenzene sodium sulfonate, fatty alcohol sodium sulfate, sodium dodecyl diphenyl oxide disulfonate, sulfonated castor oil, polyethoxyalkyl phenol sulfonate triethanolamine salt, sodium triethanolamine alkyl aryl sulfonate, magnesium lauryl sulfate, potassium lauryl sulfate, sodium lauryl ether sulfate, ammonium lauryl ether sulfate, sodium tallow sulfate, dodecylbenzene sodium sulfonate, oleyl methyl tauride, ammonium lauryl sulfate, amide sulfonate, and the like.

Other materials such as amphoteric detergent materials can be employed in formulations having a pH above the material's isoelectric point including, illustratively, the sodium salt of N-coco beta amino propionate, N-lauryl beta amine propionic acid and metal salts of substituted quaternary hydroxy cycloimidinic acid metal alcoholates such as disclosed in USP 2,528,378 to Mannheimer.

EXAMPLES

Preparation of TTA

A one liter three-necked flask is equipped with a mechanical stirrer, a thermometer and a dropping funnel. In the flask are placed 184 g. (1 mole) of undecylenic acid and 200 g. (4.35 moles) of formic acid. The stirrer is started and the reaction mixture is warmed by a water bath to 40° C. for at least one-half hour longer after all the peroxide has been added.

The reaction mixture is transferred to a suitable flask for vacuum distillation and the formic acid and any water is removed by distilling under full vacuum of the water pump. The residual hydroxyformoxyhendecanoic acid is now ready for hydrolysis. This is accomplished by boiling the mixture with 1.3 liters of 2 N sodium hydroxide. The reaction mixture is cooled after boiling for one hour and acidified to a pH of 2, or slightly lower with 6 N hydrochloric acid. After cooling well in an ice bath, the solid acid is collected on a Buchner funnel (pre-chilled), washed with ice water and sucked as dry as possible. The solid is dried in a vacuum desiccator over flake sodium hydroxide. 205.0 g. of product equal to 93.92% of the theoretical yield were obtained.

A solution of 42.78 g. (0.2 mole) of sodium metaperiodate ($NaIO_4$) in 600 ml. of 1 N sulfuric acid is prepared. In a 1 liter flask equipped with a mechanical stirrer, a thermometer and a dropping funnel are placed 40 ml. of ethanol and 43.6 g. (0.02 mole) of 10, 11-dihydroxyhendecanoic acid. This solution is warmed to 40° C. and the periodate solution is added through the separatory funnel at a rapid rate while stirring the mixture. The temperature is maintained at 40° C. for 30–40 minutes after which the solution is cooled to 20° C., and any inorganic salts that separated were collected on a Buchner funnel, sucked dry and washed with ether to remove adherent organic material.

The ether washing is used to extract the aqueous filtrate along with additional ether as may be needed. A total of three extractions with about 200 ml. of ether in each extraction should be used. The combined ether extract is shaken with a small amount of anhydrous sodium sulfate to remove most of the water, after which the ether is distilled. The residual oil is then submitted to the full vacuum of a water pump to remove any alcohol and water remaining. An oily residue sebacic semi-aldehyde, weighing 36.0 g. is obtained. (96.77% of theoretical yield.) This product is used in the next step without further purification.

18.6 g. (0.1 mole) of the sebacic semi-aldehyde is mixed with 11.45 g. (0.11 mole) of malonic acid and 10.28 g. (0.13 mole) of pyridine in a 500 ml. round bottom flask. The mixture is allowed to stand for 24 hours at room temperature and then heated for 5 hours on a steam bath. The mixture is then cooled and diluted with about 10 volumes of water. Upon acidification to pH 2 with 2 N sulfuric acid and chilled to near 0° C., the

crude 1-decene-1, 10-dicarboxylic acid is collected on a Buchaner funnel. It is sucked dry and washed with a small amount of ice cold water. Dry in a vacuum desiccator over flake caustic. The crude trans-1-decene-1,10-dicarboxylic acid, weighing 18.0 g., is recrystallized twice from boiling solvent. The yield is 11.49 g. (50.33% of theory). The melting point is 163–165° C.

Preparation of TTA cobalt salt

Three hundred milligrams of TTA were dissolved in 300 milliliters of boiling distilled water. An excess of cobalt carbonate, 250 milligrams, was added to the boiling solution, forming a pink-violet slurry. After 10 minutes of continued boiling, and filtering, the filtrate was evaporated to about 150 milliliters and let stand overnight. Two sets of crystals formed the first, on the bottom of the container, were long (1–3 millimeters) and ruby-red. The second set were colorless and floated on the filtrate liquid. The ruby-red crystals were separated by decanting the other crystals and filtrate and dried on unglazed porcelain. After recrystallization from distilled water, a yield of 90 milligrams of ruby-red powder was realized. Quantitative analysis revealed a cobalt content in the powder of 20.58%, in close agreement with a single cobalt salt of TTA (theor: 20.593%).

EXAMPLE 1

A light duty, liquid detergent was prepared.

	Percent
Ammonium linear dodecylbenzene sulfonate	15–30
Ammonium tetraethoxy secondary alcohol sulfate	7–20
Diethanol amide of lauric acid	1.5–7
Ethanol	10–20
TTA	0.0005
Water q.s. to	100

EXAMPLE 2

A solid detergent was prepared from linear sodium alkyl benzene sulfonate and sodium tripolyphosphate builder salt. About 0.0001 percent by weight, based on the total composition, of TTA was incorporated in the composition.

EXAMPLE 3

A hand soap was prepared according to commercial recipes from stearic acids saponified with sodium hydroxide except that about 1% TTA was added to the formulation.

EXAMPLE 4

Example 1 is duplicated using the TTA cobalt salt prepared above in place of the TTA.

A panel of 10 female persons is used to evaluate the product of Examples 1 and 4. A first basin is filled with normal hardness water and a capful of the Example 1 product is added. In a second basin containing the same hardness water, the same light duty detergent formulation except for the TTA or salt is dissolved, again at one capful concentration. The panel immerses one hand in the first basin and one in the second for 10 minute periods, four times daily for one week. At the end of the week, no other detergent containing water having been encountered by the test hands, the panel is asked to compare their hands. In each instance, the TTA or cobalt TTA products show substantial absence of redness and soreness as compared with the control product. The TTA cobalt salt treated hands (5) are appreciably superior to the TTA treated hands (5), but both are vastly superior to hands (10) exposed to ordinary detergent.

EXAMPLE 5

Example 4 is duplicated using sodium, potassium, manganese, copper and zinc salts in place of the cobalt salt. Results are effective in burn amelioration but to a less degree than the cobalt salt.

I claim:

1. Detergent composition consisting essentially of a synthetic organic detergent which may have a tendency to irritate skin tissue and from .00005 to 2% by weight of traumatic acid or salt of traumatic acid with a metal having an atomic number between 11 and 30 which is in one of Groups I–A, I–B, VII–B, VIII, and II–B of the Periodic Chart with the proviso that the Group VIII metal have an odd atomic number effective to counteract skin irritation.

2. Detergent composition according to claim 1 in which said detergent is dissolved in a solvent selected from the group consisting of water, lower alkanols containing 1–3 carbon atoms and mixtures thereof.

3. Detergent composition according to claim 2 in which said solvent is water.

4. Detergent composition according to claim 2 in which said solvent is a lower alkanol having up to 3 carbon atoms.

5. Detergent composition according to claim 2 in which the quantity of traumatic acid or salt is less than 1% by weight of the composition.

6. Detergent composition according to claim 2 in which said detergent is a water-soluble alkyl benzene sulfonate.

7. Detergent composition according to claim 1 in which said composition contains trans-traumatic acid.

8. Detergent composition according to claim 1 in which said composition contains a salt of traumatic acid with a metal selected from the group consisting of sodium, potassium, manganese, copper and zinc.

9. Detergent composition according to claim 1 in which said metal is cobalt.

10. Detergent composition according to claim 9 in which said salt is cobalt trans-traumatate.

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