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# (54) Soaker compositions

(57) Soaking compositions are disclosed which comprise a sorbitan ester in combination with a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent. Said compositions are diluted in water to form soaking liquors. In its broadest embodiment the present invention relates to a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition comprising such a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent, for more than 1 hour, then removed from said soaking liquor. The invention is particularly effective in removing particulate soils like silt and clay from fabrics as well as enzymatic stains.

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## Description

## Technical Field

The present invention relates to the cleaning of fabrics in soaking conditions, i.e., in conditions where the fabrics are left to soak in a soaking liquor comprising water and detergent ingredients, either as a first step before a typical washing operation, or as a single step.

## Background of the invention

Fabric soaking operations have been described in the art. In such soaking operations, fabrics are left in contact with a soaking liquor for a prolonged period of time typically ranging from more than 1 hour to overnight or even 24 hours. This laundering process has the advantage that it maximises the contact time between the fabrics and the key active ingredients of the soaking liquor. It also has the advantage that it reduces or eliminates the need for a typical laundering operation involving the need for mechanical agitation, or that it improves the efficiency of the subsequent typical laundering operation.

Such soaking operations are typically desirable to remove tough outdoor dirt from fabrics, such as particulate soil like mud, silt and/or clays. For example, clays usually have a microcrystalline mineral structure (e.g., hydrous aluminium silicate like illite, montmorillonite, kaolinite and the like) with the presence of an organic fraction. The organic fraction can contain a variety of compounds (e.g., humic acid, fulvic acid, plant/animal biomass and the like).

Clays can also contain several kinds of metals (e.g., magnesium, calcium, potassium, iron and the like). However, such particulate soil is particularly difficult to remove from fabrics. Indeed, it is believed that the very fine dirt grains like clays or silt, typically below 0.002 mm in size, can insert among fabric fibers and steadily stick to the surface of the fibers. This problem is particularly acute with socks which are most exposed to silt and clay pick-up. Also, such soaking operations are not fully satisfactory regarding the enzymatic stain removal performance. Enzymatic stains are typically composed of carbohydrates and proteinaceus soil like blood. It has now been observed that enzymatic stains may act as a glue for particulate soil on fabrics, thus removing such enzymatic stains may facilitate the removal of particulate soil from fabrics.

It is thus an object of the present invention to improve the removal of particulate soils, particularly silt, mud and/or clay, as well as enzymatic stains, from fabrics in a soaking operation.

It has been found that this object can be met by soaking fabrics in an aqueous soaking liquor comprising an effective amount of a soaking detergent composition comprising a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent, as defined hereinafter. Indeed, it has been found that a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent, in a soaking composition, delivers improved stain removal performance on tough outdoor dirt like particulate soil and/or enzymatic stains under soaking conditions (i.e., when left in contact for a prolonged period of time typically more than 1 hour up to 24 hours), as compared to the stain removal performance delivered with the same composition being free of a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent. Thus, in its broadest aspect the present invention encompasses a process of soaking fabrics, wherein said fabrics are immersed for more than one hour in a soaking liquor comprising water and an effective amount of a composition comprising a dianionic cleaning agent, as defined herein, and/or an alkoxylated dianionic cleaning agent, as defined herein, then removed from said soaking liquor.

An advantage of the present invention is that the stain removal performance, when soaking a fabric in presence of a soaking composition comprising an alkoxylated dianionic cleaning agent and/or a dianionic cleaning agent, is improved even in the presence of relatively high levels of hardness ions. Indeed, the presence of hardness ions (calcium or magnesium ions), which occur naturally in the soaking liquor, in particular, can reduce surfactant performance. Anionic surfactants are especially sensitive to hardness ions, reducing surfactant performance, eventually precipitating the surfactant from the soaking liquor as a calcium or magnesium salt. This phenomen occurs less when using a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent. Accordingly, the soaking detergent manufacturer may make use of builders which are not the more performing at sequestering free hardness ions, and thus may use less expensive builders in such a soaking composition.

Furthermore, it has been found in the preferred embodiment of the present invention that the stain removal performance on particulate soil and/or enzymatic stains is further improved by combining said dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent with a sorbitan ester, as defined hereinafter, in a soaking detergent composition. Thus, the present invention encompasses a soaking detergent composition comprising a sorbitan ester and, a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent, as defined herein, as well as a process of soaking fabrics in a soaking liquor formed with said soaking detergent composition.

An advantage of the present invention is that not only improved particulate soil removal performance is delivered but also that the soil redeposition on fabrics in prolonged soaking condition is prevented. Furthermore, the compositions of the present invention comprising said dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent together with a sorbitan ester, provide effective stain removal performance on other types of stains like greasy stains, e.g., bacon, grease, spaghetti sauce and/or bleachable stains like tea and/or coffee.

## Background art

US 3 755 201 discloses a laundry product with a blue dye stuff, surfactants, a compound selected from the group of builders, fillers, solvents and adjuvants. These compositions may be employed in pre-soaking laundry products. Polyoxyethylene sorbitan monostearate is disclosed. No dianionic cleaning agents and/or alkoxylated dianionic cleaning agents are disclosed.

US 3 762 859 discloses laundry detergent compositions comprising surfactants, and particular dyestuff. Sorbitan esters like sorbitan monolaurate, sorbitan mono-oleate and mannitan monopalmitate are disclosed. No dianionic cleaning agents and/or alkoxylated dianionic cleaning agents are disclosed.

## Summary of the invention

The present invention encompasses a soaking composition comprising:

- a sorbitan ester according to the formula $C_6H_9O_2\ (C_2H_4O)_x\ R_1R_2R_3$, wherein x is an integer of from 0 to 40, $R_1$, $R_2$ are independently OH or $(C_n\ H_{n+1})COO$, and $R_3$ is $(C_n\ H_{n+1})COO$ group, where n is an integer of from 11 to 17; and

- a dianionic cleaning agent comprising a structural skeleton of at least five carbon atoms to which two anionic substituent groups spaced at least three atoms apart are attached, wherein one anionic substituent group is a sulfate group and the other anionic substituent is selected from sulfate and sulfonate, and/or

- an alkoxylated dianionic cleaning agent comprising a structural skeleton of at least five carbon atoms to which two anionic substituent groups spaced at least three atoms apart are attached, wherein one anionic substituent group is an alkoxy-linked sulfate group and the other anionic substituent is selected from sulfate and sulfonate, optionally alkoxy-linked.

The present invention further encompasses a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition as described hereinabove, for an effective period of time, then removed from said soaking liquor. In its broadest aspect the present invention encompasses a process of soaking fabrics, wherein said fabrics are immersed for more than one hour in a soaking liquor comprising water and an effective amount of a composition comprising a dianionic cleaning agent, as defined herein, and/or an alkoxylated dianionic cleaning agent, as defined herein, then removed from said soaking liquor.

## Detailed Description of the invention

The present invention encompasses a composition and a process of soaking fabrics. The composition, hereinafter referred to as the soaking composition is used in the soaking process.

### *A - The composition:*

The present invention encompasses a composition which comprises a sorbitan ester, and a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent.

The sorbitan ester:

Accordingly, the first essential ingredient of the compositions of the present invention is a sorbitan ester according to the formula $C_6H_9O_2\ (C_2H_4O)_x\ R_1R_2R_3$, wherein x is an integer of from 0 to 40, $R_1$, $R_2$ are independently OH or $(C_n\ H_{n+1})COO$, and $R_3$ is $(C_n\ H_{n+1})COO$ group, where n is an integer of from 11 to 17.

In the preferred compositions herein, x is 0 or 20, and the most preferred compositions herein comprise polyethoxylated (20) sorbitan tristearate, i.e. $C_6H_9O_2\ (C_2H_4O)_{20}\ (C_{17}\ H_{35}COO)_3$, or polyethoxylated (20) sorbitan monostearate, i.e. $C_6H_9O_2\ (C_2H_4O)_{20}(OH)_2(C_{17}\ H_{35}COO)$, or sorbitan monostearate, i.e. $C_6H_9O_2(OH)_2(C_{17}\ H_{35}COO)$, or sorbitan monopalmitate, i.e. $C_6H_9O_2(OH)_2(C_{15}\ H_{31}COO)$, or mixtures thereof.

All these materials are commercially available under several trade names, such as Glycosperse TS 20 from Lonza (polyethoxylated sorbitan tristearate), Glycosperse S 20 from Lonza (polyethoxylated sorbitan monostearate), Radiasurf 7145 from Fina (sorbitan monostearate), Radiasurf 7135 from Fina (sorbitan monopalmitate), Armotan MP from Akzo (sorbitan monopalmitate).

It has further been found that combining ethoxylated sorbitan esters with non-ethoxylated sorbitan esters provides better performance than either kind alone.

In the soaking composition herein, there should be from 0.01% to 10% of the total composition of said sorbitan ester or mixtures thereof, preferably from 0.01% to 5%, most preferably from 0.5% to 5%.

The second essential ingredient of the compositions of the present invention is a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent.

## The dianionic cleaning agent

The dianionic cleaning agent comprises a structural skeleton of at least five carbon atoms, to which two anionic substituent groups spaced at least three atoms apart are attached. At least one of said anionic substituent groups is a sulfate group; the other is a sulfate or sulfonate group, preferably a sulfate group. Said structural skeleton can for example comprise any of the groups consisting of alkyl, substituted alkyl, alkenyl, aryl, alkaryl, ether, ester, amine and amide groups.

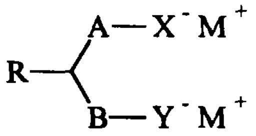
The structural skeleton preferably comprises from 5 to 32, preferably 7 to 28, most preferably 12 to 24 atoms. Preferably the structural skeleton comprises only carbon-containing groups and more preferably comprises only hydrocarbyl groups. Most preferably the structural skeleton comprises only straight or branched chain alkyl groups.

The structural skeleton is preferably branched. Preferably at least 10 % by weight of the structural skeleton is branched and the branches are preferably from 1 to 5, more preferably from 1 to 3, most preferably from 1 to 2 atoms in length (not including the sulfate or sulfonate group attached to the branching).

Again, the anionic substituent groups present in the dianionic cleaning agents useful herein are spaced at a distance of at least three atoms from each other. For example, where one anionic substituent group is attached to a carbon (the first carbon), said first carbon is attached to a second carbon, which is in turn, attached to a third carbon and the third carbon is attached to the second anionic substituent group to give a spacing of three carbon atoms.

In a preferred aspect of the present invention, at least one anionic substituent group is substituted at a primary position on the structural skeleton. The anionic substituent groups are preferably spaced 1-3, 1-4, 1-5, 1-6 or greater apart; a 1-4 substitution for disulfated compounds is most preferred, and 1-4 and 1-5 substitution for sulfated/sulfonated compounds is most preferred. For full clarity, the term 1-n substitution is to be interpreted such that 1 indicates an anionic substituent group located at a given position on the structural skeleton and n indicates the number of atoms spaced between the first and second anionic substituent groups.

A preferred dianionic cleaning agent has the formula



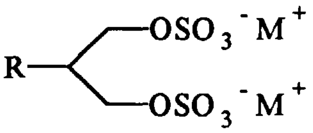
where R is an alkyl, substituted alkyl, alkenyl, aryl, alkaryl, ether, ester, amine or amide group of chain length $C_1$ to $C_{28}$, preferably $C_3$ to $C_{24}$, most preferably $C_8$ to $C_{20}$, or hydrogen; A and B are independently selected from alkyl, substituted alkyl, and alkenyl groups of chain length $C_1$ to $C_{28}$, preferably $C_1$ to $C_5$, most preferably $C_1$ or $C_2$, or a covalent bond, and A and B in total contain at least 2 atoms; A, B, and R in total contain from 4 to 31 carbon atoms; X and Y are anionic groups selected from the group consisting of sulfate and sulfonate, provided that at least one of X or Y is a sulfate group; and M is a cationic moiety, preferably a substituted or unsubstituted ammonium ion, or an alkali or alkaline earth metal ion.

The most preferred dianionic cleaning agent has the formula as above where R is an alkyl group of chain length from $C_{10}$ to $C_{18}$, A and B are independently $C_1$ or $C_2$, both X and Y are sulfate groups, and M is a potassium, ammonium, or a sodium ion.

The dianionic cleaning agent is typically present at levels of incorporation of from 0.01% to 50%, preferably from 0.05% to 10%, more preferably from 0.1% to 5%, and most preferably from 0.2% to 2% by weight of the soaking composition.

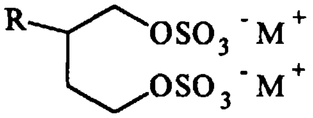
Preferred dianionic cleaning agents herein include:

(a) 1,3 disulfate compounds, preferably 1,3 C7-C23 (i.e., the total number of carbons in the molecule) straight or branched chain alkyl or alkenyl disulfates, more preferably having the formula:



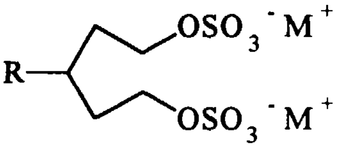
wherein R is a straight or branched chain alkyl or alkenyl group of chain length from $C_4$ to $C_{18}$;

(b) 1,4 disulfate compounds, preferably 1,4 C8-C22 straight or branched chain alkyl or alkenyl disulfates, more preferably having the formula:



wherein R is a straight or branched chain alkyl or alkenyl group of chain length from $C_4$ to $C_{18}$; preferred R are selected from octanyl, nonanyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, and mixtures thereof; and

(c) 1,5 disulfate compounds, preferably 1,5 C9-C23 straight or branched chain alkyl or alkenyl disulfates, more preferably having the formula:



wherein R is a straight or branched chain alkyl or alkenyl group of chain length from $C_4$ to $C_{18}$.

As will be appreciated more fully from the following discussion of preferred synthesis methods, the present invention compositions may also comprise some amount of sulfated alcohols and/or sulfonated alcohols which may comprise (to differing degrees depending on the reaction conditions used) a portion of the dianionic cleaning agent raw material used to manufacture the present invention compositions. Such alcohols are typically compatible with the present invention compositions and may be present as long as the requisite amount of dianionic cleaning agent is present in the final composition.

## Synthesis Methods:

Known syntheses of certain disulfated surfactants, in general, use an alkyl or alkenyl succinic anhydride as the principal starting material. This is initially subjected to a reduction step from which a diol is obtained. Subsequently the diol is subjected to a sulfation step to give the disulfated product. As an example, US-A-3,634,269 describes 2-alkyl or alkenyl-1,4-butanediol disulfates prepared by the reduction of alkenyl succinic anhydrides with lithium aluminium hydride to produce either alkenyl or alkyl diols which are then sulfated. In addition, US-A-3,959,334 and US-A-4,000,081 describe 2-hydrocarbyl-1,4-butanediol disulfates also prepared using a method involving the reduction of alkenyl succinic anhydrides with lithium aluminium hydride to produce either alkenyl or alkyl diols which are then sulfated. See also US-A-3,832,408 and US-A-3,860,625 which describe 2-alkyl or alkenyl-1,4-butanediol ethoxylate disulfates prepared by the reduction of alkenyl succinic anhydrides with lithium aluminium hydride to produce either alkenyl or alkyl diols which are then ethoxylated prior to sulfation.

These compounds may also be made by a method involving synthesis of the disulfated cleaning agent from a substituted cyclic anhydride having one or more carbon chain substituents having in total at least 5 carbon atoms comprising the following steps:

(i) reduction of said substituted cyclic anhydride to form a diol; and
(ii) sulfation of said diol to form a disulfate

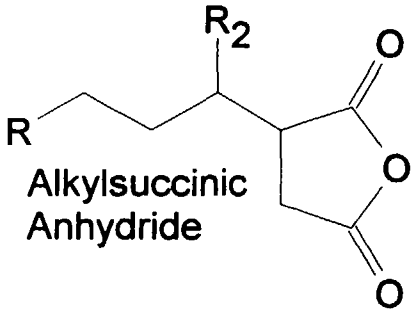
wherein said reduction step comprises hydrogenation under pressure in the presence of a transition metal-containing hydrogenation catalyst.

The cyclic anhydride starting material has a ring structure and comprises an acid anhydride linkage. Cyclic anhydrides are generally formed by a ring forming condensation reaction of a single organic compound having a first carboxylic acid (-COOH) functional group and a second -COY functional group separated from the carboxylic acid functional group by at least two carbon atoms, wherein Y is usually an -OH, or halogen functionality.

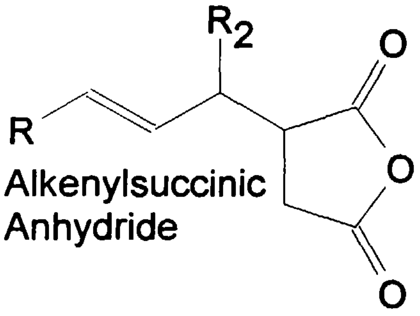
A specific example of an organic compound which may be condensed to form a cyclic anhydride is maleic acid which on self-condensation provides maleic anhydride. Maleic anhydride is readily available commercially. The ring structure of the cyclic anhydride starting material contains from 4 to 7 carbon atoms, preferably from 4 to 6 carbon atoms in the ring structure. Most preferably the cyclic anhydride starting material is based on succinic anhydride which has a 5-membered ring structure containing 4 carbon atoms in the ring.

The cyclic anhydride starting material is substituted by one or more carbon containing substituents, such that in total, these substituents contain at least 5 carbon atoms, preferably from 5 to 25 carbon atoms, more preferably from 7 to 21 carbon atoms. Preferably, all of the carbon chain substituent(s) comprise either alkyl or alkenyl chains, which may be branched or unbranched. In one preferred aspect they are essentially unbranched. In another preferred aspect the chains are primarily monobranched, that is more than 50% by weight of the chains are monobranched. In one preferred aspect the substituted cyclic anhydride has a single carbon chain substituent. In another preferred aspect the substituted cyclic anhydride has two carbon chain substituents each having different points of attachment to the ring structure.

Substituted alkenylsuccinic and alkylsuccinic anhydrides are suitable starting materials herein. Preferred anhydrides of this type have the following structures:



Alkylsuccinic Anhydride



Alkenylsuccinic Anhydride

where R and $R_2$ are either H or an alkyl group. In one preferred aspect $R_2$ is H.

Linear alkenylsuccinic anhydrides may be obtained in high yield from the single stage 'ene reaction' of maleic anhydride with an alpha-olefin. Branched alkenylsuccinic anhydrides may be obtained from the single stage 'ene reaction' of maleic anhydride with an internal olefin, such as those obtainable from the familiar SHOP (tradename of the Shell Corporation) olefin making process.

Alkylsuccinic anhydride starting materials can be made by reducing alkenylsuccinic anhydrides. This reduction can be achieved under the conditions of the catalytic hydrogenation reduction step as described herein.

The first step is the reduction of the substituted cyclic anhydride to form a diol. The reduction step comprises hydrogenation under pressure in the presence of a transition metal-containing hydrogenation catalyst.

It is an advantage of this method that under the conditions of the catalytic hydrogenation reduction step any alkene linkages are also reduced to alkyl linkages. Thus, if an alkenylsuccinic anhydride is used as the starting material it is reduced via a (single) reduction step to the diol having alkyl chain substituents, as are desired. This contrasts with the situation where $LiAlH_4$, which does not reduce alkene linkages, is used in the reduction step, wherein an extra step involving the reduction of the alkenyl succinic anhydride to the alkyl succinic anhydride (via e.g. Pd/hydrogen) must be employed to obtain the desired diol product.

The hydrogenation catalyst acts functionally to enhance the efficiency of the reductive hydrogenation process. For use on a commercial scale it is desirable that the catalyst is easy to regenerate. Preferably, the catalyst contains a transition metal selected from the group consisting of the group VIA (particularly Cr), VIIA (particularly Mn), VIII (particularly

Fe, Co, Ni, Ru, Rh, Pd, Pt) and IB (particularly Cu) elements. Catalysts containing mixtures of any of these transition metals are envisaged as are catalysts containing other metals including the alkali and alkaline earth metals. Platinum, paladium, and copper-containing catalysts, particularly copper chromite (which is commercially available and relatively easy to regenerate) are most preferred. An alternate synthesis may also utilize supported Pd/Rh catalysts to selectively hydrogenate maleic anhydride to either THF of butane diol, as described by S.B. Ziernecki, C&EN, April 3, 1995, pp 20-23.

The hydrogenation catalyst may advantageously be supported on an inert support material. The support material can generally comprise an oxide salt comprising a metal selected from the group consisting of aluminium, silicon and any mixtures thereof. Supports comprising aluminium oxide or silicon dioxide are especially preferred. Carbon and clay materials are also suitable supports.

The reductive hydrogenation step is carried out under pressure, and generally at elevated temperature. Usually a solvent is employed. This step can be carried out by a batch, continuous or vapor-phase process. A continuous process is preferred. The pressure is typically from $1 \times 10^5$ to $1 \times 10^7$ Pa, more preferably from $1 \times 10^6$ to $5 \times 10^6$ Pa. The temperature is generally from 150°C to 350°C, more preferably from 200°C to 300°C. The time of reaction is generally from 30 minutes to 10 hours. Suitable solvents include alcohols, particularly methanol, ethanol, propanol and butanol.

It is to appreciated that the exact process conditions used for any particular synthesis will be varied to achieve optimum results in accord with the usual process optimization steps which will be within the remit of the skilled person. In particular the process conditions will be adjusted to minimise the occurrence of any competing side-reactions.

One possible problem derives from the incomplete reduction of the cyclic anhydride, such that lactones are formed. These are however, convertible to diols by further catalytic hydrogenation. It may be advantageous to carry out the hydrogenation in two steps, preferably as part of a continuous step-wise process, such that a lactone is formed in the first step followed by a second step in which the lactone is reduced to the diol. Conditions which favour lactone formation are high temperature (~300 °C) and low pressures ($\sim 1 \times 10^5$ Pa). Any water formed during the hydrogenation will primarily be in the vapour phase, so that the anhydride is unlikely to be converted into a carboxylic acid which can inhibit the catalyst. The best conditions for diol formation from the lactone are lower temperatures (~220 °C) and high pressures ($\sim 1 \times 10^7$ Pa), both of which conditions minimise the production of furan by-product.

Furans can be formed by a ring closure reaction of the diol product. The tendency for such furans to form is greater at higher reaction temperatures and can be promoted by the transition-metal containing catalysts employed in the reduction step. The formation of furans may therefore be minimised by the use of lower reaction temperatures and by designing the process such that once formed the diol is removed from the catalytic environment. The latter objective is met by the use of a continuous process whereby the reactants contact a high level of catalyst for a relatively short time and are then removed from the catalytic environment. By optimization of the time of contact with the catalyst the formation of the desired diol is maximised and that of the furan by-product minimised.

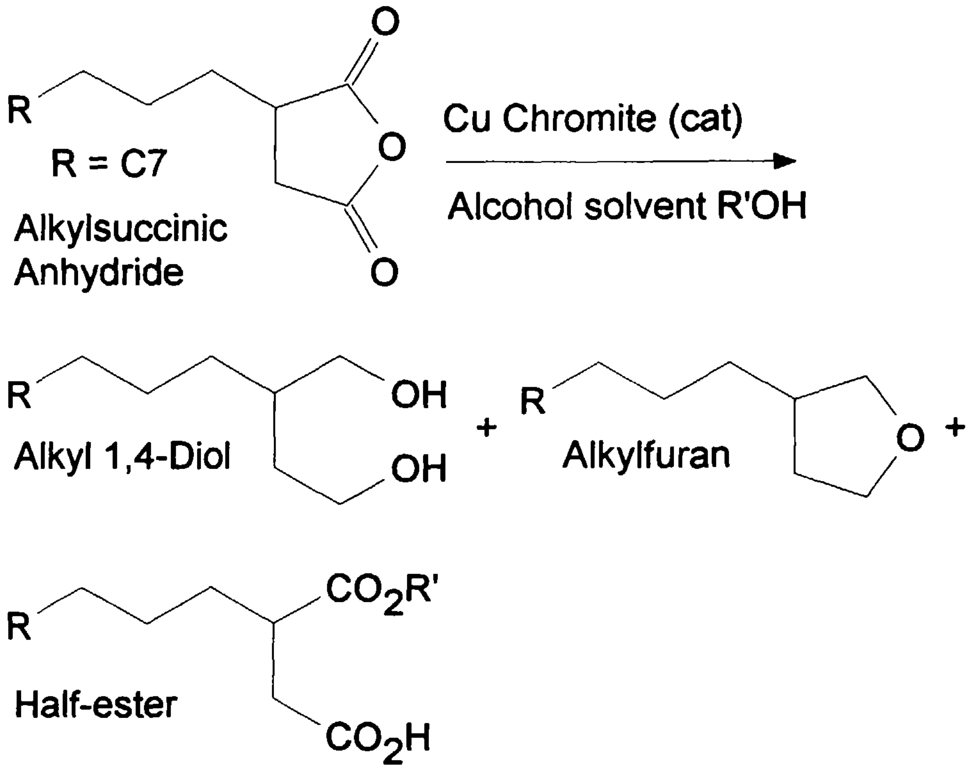
The presence of acids promotes furan formation. In particular, carboxylic acids which may be formed by certain ring-opening reactions of the cyclic anhydrides under the conditions of the reduction step can promote furan formation. This problem can be alleviated by first forming the lactone in a separate step as mentioned above or by the use of an additional esterification step in which the cyclic anhydride is first treated with an alcohol, particularly methanol, in the presence of an esterification catalyst to form a diester. The diester is then converted to the diol via the reduction step.

The sulfation step may be carried out using any of the sulfation steps known in the art, including for example those described in US-A-3,634,269, US-A-3,959,334 and US-A-4,000,081. In particular the sulfation may be carried out in two stages where the first stage involves treatment of the diol with a sulfation agent, generally selected from the group consisting of chlorosulfonic acid, sulfur trioxide, adducts of sulfur trioxide with amines and any mixtures thereof. The second stage involves neutralization, which is generally carried out using NaOH.

## Synthesis Example I - C14 alkyl-1,4-disulfate

Decyl succinic anhydride as shown in the reaction scheme below (R = a heptyl group) is employed as the starting material. This material is obtained by hydrogenation in the presence of a Pd catalyst of the alkenyl succinic anhydride product obtained from the 'ene' reaction of maleic (acid) anhydride with dec-1-ene.

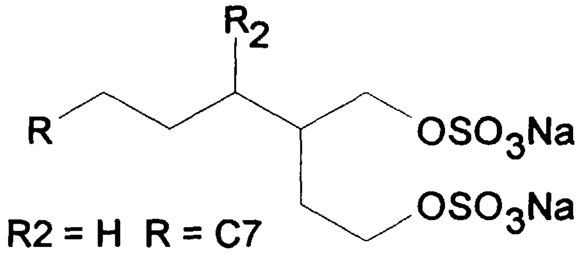
The general reaction scheme for the reduction step is as outlined below:



It should be noted from the above that both furan and half ester by-products can also be formed in the reaction. The reactor utilized is an electrically heated 500 ml (39 mm internal diameter x 432 mm internal length) Autoclave Engineers type 316 (tradename) stainless steel rocking autoclave fitted with an internal thermocouple and valving for periodic sampling of reaction mixtures. The reactor is charged with 50 ml of alcohol solvent and 5 grams of copper chromite catalyst, as sold by Engelhardt under the tradename CU-1885P, that had been washed several times with high purity water, then several times with alcohol solvent. The reactor and contents are then heated to 250°C at a hydrogen pressure of $2.4 \times 10^6$ Pa and held for 1 hour. The reactor is then cooled and charged (without exposing the catalyst to air) with 20 grams of the cyclic anhydride starting material and an additional 50 ml of alcohol solvent. The process is carried out under different conditions of pressure and temperature, and with varying reaction times. Details of different reaction conditions are summarised in the table below:

| Example No. | Pressure ($10^6$Pa) | Temp. (°C) | Time | Solvent |
|---|---|---|---|---|
| | | | | |
| 1 | 2.8 | 235 | 2.1 hr | 1-butanol |
| 2 | 2.1 | 210 | 48 hr | 1-butanol |
| 3 | 2.85 | 250 | 2.5 hr | 1-butanol |
| 4 | 2.1 | 250 | 15 hr | methanol |
| 5 | 2.1 | 300 | 15 hr | methanol |
| 6 | 2.1 | 200 | 15 hr | 1-octanol |
| 7 | 2.1 | 192 | 4.5 days | isobutanol |
| 8 | 2.1 | 187 | 2.5 days | ethylene glycol |

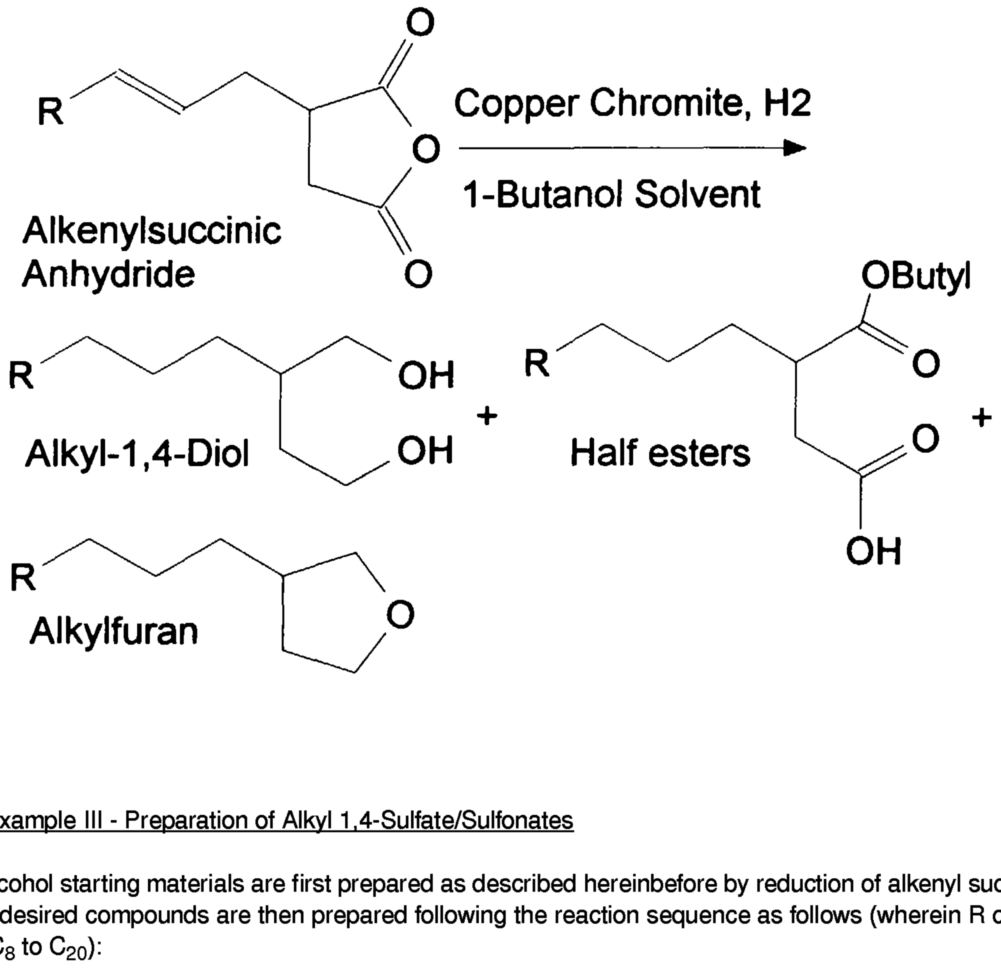
The sulfation step is carried out, in each case, on the 1,4-alkyl diol product obtained from the reduction step. Chlorosulfonic acid is used which results in a high yield (typically > 90%) of the required $C_{14}$ alkyl 1,4 disulfate end-product as shown below:



## Synthesis Example II - C14 alkyl-1,4-disulfate

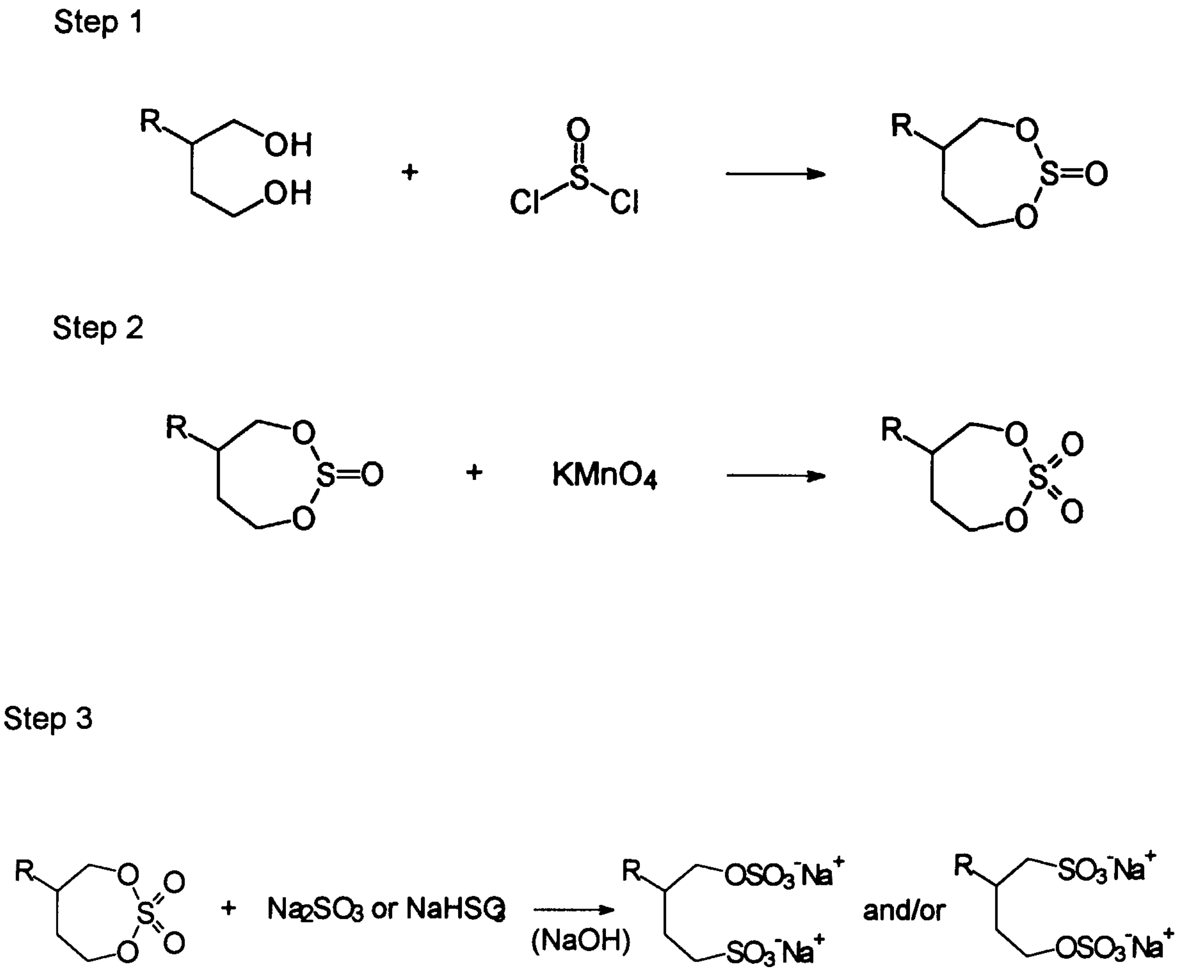
The alkenyl succinic anhydride product obtained from the 'ene' reaction of maleic (acid) anhydride with dec-1-ene (i.e. R = a heptyl group) is used directly as the cyclic anhydride starting material. The need for the additional 'pre-step' of reduction of the alkenyl succinic anhydride to an alkyl succinic anhydride is thus avoided. All other method steps are as in Synthesis Example I.

The reaction scheme for the reduction step is thus as shown below:



## Synthesis Example III - Preparation of Alkyl 1,4-Sulfate/Sulfonates

1,4-dialcohol starting materials are first prepared as described hereinbefore by reduction of alkenyl succinic anhydrides. The desired compounds are then prepared following the reaction sequence as follows (wherein R can be alkyl or alkenyl, $C_8$ to $C_{20}$):



This reaction scheme is described in part in greater detail in Berridge, et. al., (J. Org. Chem. 1990, 55, 1211). This paper illustrates Steps 1 and 2 for several 1,2-, 1,3-, and 1,4-dialcohols, and also illustrates the opening of cyclic sulfates with phenoxide and fluoride anions. Thus, this reaction sequence is not limited to the preparation of 1,4-sulfate/sulfonates, but may also be followed for the preparation of 1,3-sulfate/sulfonates from the corresponding 1,3-dialcohols.

## The alkoxylated dianionic cleaning agent

The alkoxylated dianionic cleaning agent to be used herein comprises a structural skeleton of at least five carbon atoms, to which two anionic substituent groups spaced at least three atoms apart are attached. At least one of said anionic substituent groups is an alkoxy-linked sulfate group; the other is a sulfate or sulfonate group, preferably a sulfate group linked by alkoxy moieties to the carbon structural skeleton. Said structural skeleton can for example comprise any of the groups consisting of alkyl, substituted alkyl, alkenyl, aryl, alkaryl, ether, ester, amine and amide groups. Preferred alkoxy moieties are ethoxy, propoxy, and combinations thereof.

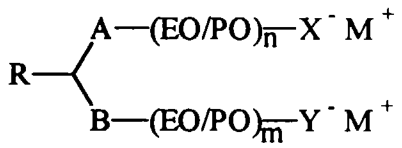
The structural skeleton preferably comprises from 5 to 32, preferably 7 to 28, most preferably 12 to 24 atoms. Preferably the structural skeleton comprises only carbon-containing groups and more preferably comprises only hydrocarbyl groups. Most preferably the structural skeleton comprises only straight or branched chain alkyl groups.

The structural skeleton is preferably branched. Preferably at least 10 % by weight of the structural skeleton is branched and the branches are preferably from 1 to 5, more preferably from 1 to 3, most preferably from 1 to 2 atoms in length (not including the sulfate or sulfonate group attached to the branching).

Again, the anionic substituent groups (which for purposes of counting positions along the structural skeleton includes the alkoxy linking moieties) present in the alkoxylated dianionic cleaning agents useful herein are spaced at a distance of at least three atoms from each other. For example, where one anionic substituent group is attached to a carbon (the first carbon), said first carbon is attached to a second carbon, which is in turn, attached to a third carbon and the third carbon is attached to the second anionic substituent group to give a spacing of three carbon atoms.

In a preferred aspect of the present invention, at least one alkoxy-linked anionic substituent group is substituted at a primary position on the structural skeleton. The anionic substituent groups are preferably spaced 1-3, 1-4, 1-5, 1-6 or greater apart; a 1-4 substitution for disulfated compounds is most preferred. For full clarity, the term 1-n substitution is to be interpreted such that 1 indicates an anionic substituent group (including any alkoxy linking moieties) located at a given position on the structural skeleton and n indicates the number of atoms spaced between the first and second anionic substituent groups (including any alkoxy linking moieties).

A preferred alkoxylated dianionic cleaning agent has the formula

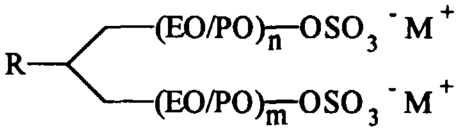


where R is an alkyl, substituted alkyl, alkenyl, aryl, alkaryl, ether, ester, amine or amide group of chain length $C_1$ to $C_{28}$, preferably $C_3$ to $C_{24}$, most preferably $C_8$ to $C_{20}$, or hydrogen; A and B are independently selected from alkyl, substituted alkyl, and alkenyl group of chain length $C_1$ to $C_{28}$, preferably $C_1$ to $C_5$, most preferably $C_1$ or $C_2$, or a covalent bond; EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein n and m are independently within the range of from 0 to 10, with at least m or n being at least 1; A and B in total contain at least 2 atoms; A, B, and R in total contain from 4 to 31 carbon atoms; X and Y are anionic groups selected from the group consisting of sulfate and sulfonate, provided that at least one of X or Y is a sulfate group; and M is a cationic moiety, preferably a substituted or unsubstituted ammonium ion, or an alkali or alkaline earth metal ion.

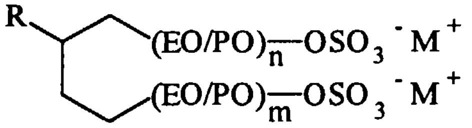
The most preferred alkoxylated dianionic cleaning agent has the formula as above where R is an alkyl group of chain length from $C_{10}$ to $C_{18}$, A and B are independently $C_1$ or $C_2$, n and m are both 1, both X and Y are sulfate groups, and M is a potassium, ammonium, or a sodium ion.

The alkoxylated dianionic cleaning agent is typically present at levels of incorporation of from 0.01% to 50%, preferably from 0.05% to 10%, more preferably from 0.1% to 5%, and most preferably from 0.2% to 2% by weight of the soaking composition.

Preferred alkoxylated dianionic cleaning agents herein include ethoxylated and/or propoxylated disulfate compounds, preferably C10-C24 straight or branched chain alkyl or alkenyl ethoxylated and/or propoxylated disulfates, more preferably having the formulae:



and



wherein R is a straight or branched chain alkyl or alkenyl group of chain length from C6 to $C_{18}$; EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups; and n and m are independently within the range of from 0 to 10 (preferably from 0 to 5), with at least m or n being 1.

As will be appreciated more fully from the following discussion of preferred synthesis methods, the present invention compositions may also comprise some amount of sulfated alcohols and/or sulfonated alcohols which may comprise (to differing degrees depending on the reaction conditions used) a portion of the alkoxylated dianionic cleaning agent raw material used to manufacture the present invention compositions. Such alcohols are typically compatible with the present invention compositions and may be present as long as the requisite amount of alkoxylated dianionic cleaning agent is present in the final composition.

Synthesis Methods:

Known syntheses of certain disulfated surfactants, in general, use an alkyl or alkenyl succinic anhydride as the principal starting material. This is initially subjected to a reduction step from which a diol is obtained. Subsequently the diol is alkoxylated and then subjected to a sulfation step to give the alkoxylated disulfated product. As an example, US-A-

3,832,408 and US-A-3,860,625 describe 2-alkyl or alkenyl-1,4-butanediol ethoxylate disulfates prepared by the reduction of alkenyl succinic anhydrides with lithium aluminum hydride to produce either alkenyl or alkyl diols which are then ethoxylated prior to sulfation. See also US-A-3,634,269 describes 2-alkyl or alkenyl-1,4-butanediol disulfates prepared by the reduction of alkenyl succinic anhydrides with lithium aluminum hydride to produce either alkenyl or alkyl diols which are then sulfated. In addition, US-A-3,959,334 and US-A-4,000,081 describe 2-hydrocarbyl-1,4-butanediol disulfates also prepared using a method involving the reduction of alkenyl succinic anhydrides with lithium aluminum hydride to produce either alkenyl or alkyl diols which are then sulfated.

These compounds may also be made by a method involving synthesis of the disulfated cleaning agent from a substituted cyclic anhydride having one or more carbon chain substituents having in total at least 5 carbon atoms comprising the following steps:

(i) reduction of said substituted cyclic anhydride to form a diol;
(ii) alkoxylation of said diol to form an alkoxylated diol; and
(iii) sulfation of said alkoxylated diol to form a disulfate

wherein said reduction step comprises hydrogenation under pressure in the presence of a transition metal-containing hydrogenation catalyst.

In this synthesis method of an alkoxylated dianionic cleaning agent herein the starting material, i.e., said substituted cyclic anhydride, as well as the reduction of said starting material to form a diol may be performed as for the synthesis method of a dianionic cleaning agent described herein before.

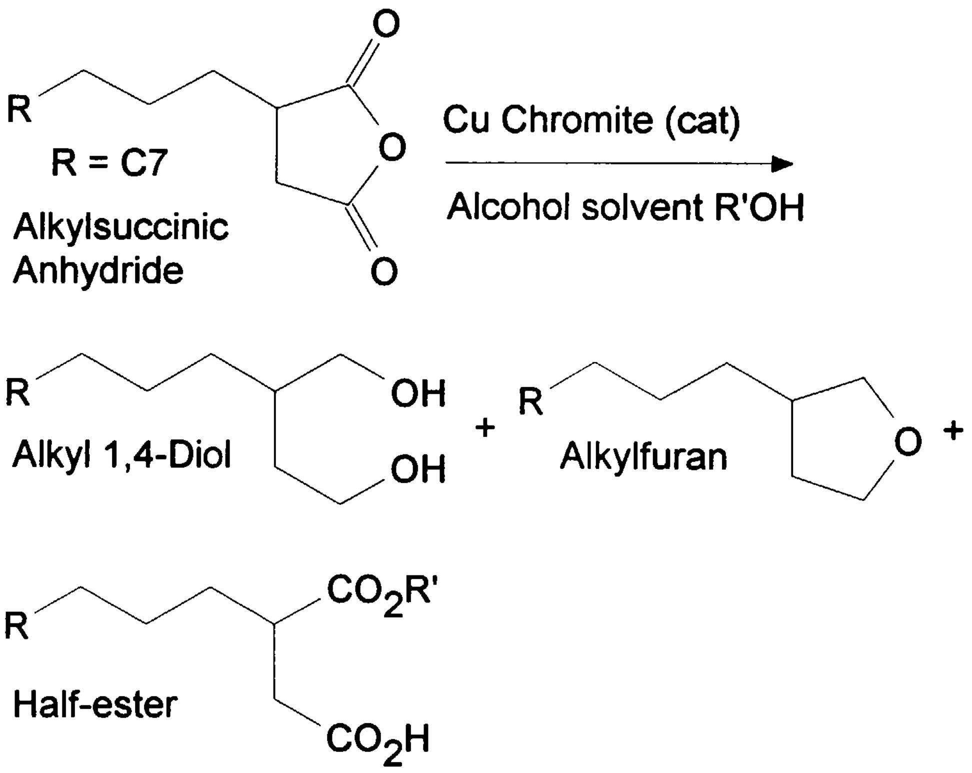
Once obtained, the diol is then alkoxylated prior to the sulfation step, such that alkoxylated disulfate cleaning agents are obtained as the final product. Suitable methods for the alkoxylation of diols are described in US Patents 3,832,408 and 3,860,625 noted hereinbefore. The condensation products of the diols with from 1 to 25 moles, preferably from 2 to 10 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are preferred herein.

The sulfation step may be carried out using any of the sulfation steps known in the art as already described hereinbefore in the synthesis method of the dianionic cleaning agents herein.

Synthesis Example I - C14 alkyl-1,4-ethoxylate disulfate

Decyl succinic anhydride as shown in the reaction scheme below (R = a heptyl group) is employed as the starting material. This material is obtained by hydrogenation in the presence of a Pd catalyst of the alkenyl succinic anhydride product obtained from the 'ene' reaction of maleic (acid) anhydride with dec-1-ene.

The general reaction scheme for the reduction step is as outlined below:



It should be noted from the above that both furan and half ester by-products can also be formed in the reaction.

The reactor utilized is an electrically heated 500 ml (39 mm internal diameter x 432 mm internal length) Autoclave Engineers type 316 (tradename) stainless steel rocking autoclave fitted with an internal thermocouple and valving for periodic sampling of reaction mixtures. The reactor is charged with 50 ml of alcohol solvent and 5 grams of copper chromite catalyst, as sold by Engelhardt under the tradename CU-1885P, that had been washed several times with high purity water then several times with alcohol solvent. The reactor and contents are then heated to 250°C at a hydrogen pressure of 2.4 x $10^6$ Pa and held for 1 hour. The reactor is then cooled and charged (without exposing the catalyst to air) with 20 grams of the cyclic anhydride starting material and an additional 50 ml of alcohol solvent. The process is carried out under different conditions of pressure and temperature, and with varying reaction times. Details of different reaction conditions are summarised in the table below:

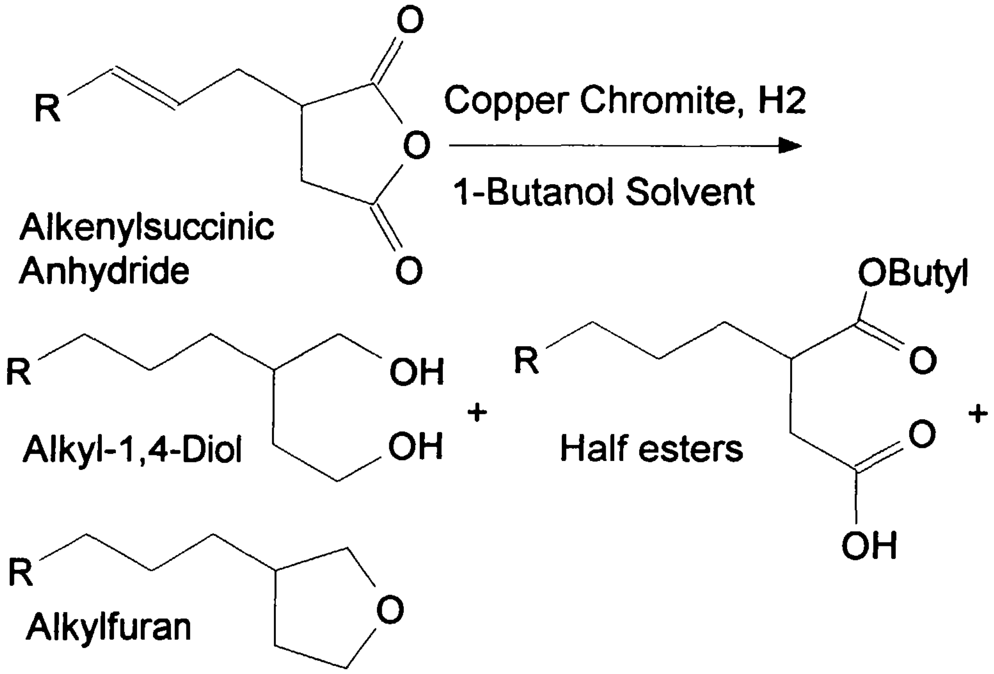
| Example No. | Pressure ($10^6$Pa) | Temp. (°C) | Time | Solvent |
|---|---|---|---|---|
| | | | | |
| 1 | 2.8 | 235 | 2.1 hr | 1-butanol |
| 2 | 2.1 | 210 | 48 hr | 1-butanol |
| 3 | 2.85 | 250 | 2.5 hr | 1-butanol |
| 4 | 2.1 | 250 | 15 hr | methanol |
| 5 | 2.1 | 300 | 15 hr | methanol |
| 6 | 2.1 | 200 | 15 hr | 1-octanol |
| 7 | 2.1 | 192 | 4.5 days | isobutanol |
| 8 | 2.1 | 187 | 2.5 days | ethylene glycol |

This diol is then treated with an excess of ethylene oxide to give the ethoxylated diol. The sulfation step is then carried out, in each case, on the 1,4-alkyl diol product obtained from the reduction step. Chlorosulfonic acid is used which results in a high yield (typically > 90%) of the required $C_{14}$ alkyl 1,4 ethoxylated disulfate end-product.

Synthesis Example II - C14 alkyl-1,4-ethoxylate disulfate

The alkenyl succinic anhydride product obtained from the 'ene' reaction of maleic (acid) anhydride with dec-1-ene (i.e. R = a heptyl group) is used directly as the cyclic anhydride starting material. The need for the additional 'pre-step' of reduction of the alkenyl succinic anhydride to an alkyl succinic anhydride is thus avoided. All other method steps are as in Synthesis Example I.

The reaction scheme for the reduction step is thus as shown below:



Optional ingredients:

As an optional but highly preferred ingredient, the compositions according to the present invention may further comprise an oxygen bleach. Indeed, oxygen beaches provide a multitude of benefits such as bleaching of stains, deodorization, as well as disinfectancy, and the sorbitan esters and (alkoxylated) dianionic cleaning agents according to the present invention have a further particular advantage that they are resistant to oxydation by oxygen bleaches. The oxygen bleach in the composition may come from a variety of sources such as hydrogen peroxide or any of the addition compounds of hydrogen peroxide, or organic peroxyacid, or mixtures thereof. By addition compounds of hydrogen peroxide it is meant compounds which are formed by the addition of hydrogen peroxide to a second chemical compound, which may be for example an inorganic salt, urea or organic carboxylate, to provide the addition compound. Examples of the addition compounds of hydrogen peroxide include inorganic perhydrate salts, the compounds hydrogen peroxide forms with organic carboxylates, urea, and compounds in which hydrogen peroxide is clathrated.

Other suitable oxygen beaches include persulphates, particularly potassium persulphate $K_2S_2O_8$ and sodium persulphate $Na_2S_2O_8$. Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts.

The alkali metal salt of percarbonate, perborate or mixtures thereof, are the preferred inorganic perhydrate salts for use herein. Preferred alkali metal salt of percarbonate is sodium percarbonate.

Soaking compositions in the present invention may comprise from 0.01% to 80% by weight of the total composition of an oxygen bleach or mixtures thereof, preferably from 5% to 45% and more preferably from 10% to 40%.

When the soaking compositions herein comprise an oxygen bleach, it is preferred for them to further comprise bleach activators typically up to a level of 30% by weight of the total composition. Examples of suitable compounds of this type are disclosed in British Patent GB 1 586 769 and GB 2 143 231. Preferred examples of such compounds are tetracetyl ethylene diamine, (TAED), sodium 3, 5, 5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and n-nonanoyloxybenzenesulphonate (NOBS), and acetyl triethyl citrate (ATC) such as described in European patent application 91870207.7. Also particularly preferred are N-acyl caprolactam selected from the group consisting of substituted or unsubstituted benzoyl caprolactam, octanyl caprolactam, nonanoyl caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl caprolactam, butanoyl caprolactam pentanoyl caprolactam. The soaking compositions herein may comprise mixtures of said bleach activators.

Preferred mixtures of bleach activators herein comprise n-nonanoyloxybenzenesulphonate (NOBS) together with a second bleach activator having a low tendency to generate diacyl peroxide, but which delivers mainly peracid. Said second bleach activators may include tetracetyl ethylene diamine (TAED), acetyl triethyl citrate (ATC), acetyl caprolactam, benzoyl caprolactam and the like, or mixtures thereof. Indeed, it has been found that mixtures of bleach activators comprising n-nonanoyloxybenzenesulphonate and said second bleach activators, allow to boost particulate soil cleaning performance while exhibiting at the same time good performance on diacyl peroxide sensitive soil (e.g. beta-carotene) and on peracid sensitive soil (e.g. body soils).

Accordingly, the soaking compositions herein may comprise from 0% to 15% by weight of the total composition of n-nonanoyloxybenzenesulphonate, preferably from 1% to 10% and more preferably from 3% to 7% and from 0% to 15% by weight of the total composition of said second bleach activator preferably from 1% to 10% and more preferably from 3% to 7%.

The compositions herein may comprise an acidifying system amongst the preferred optional ingredients. The purpose of said acidifying system is to control the alkalinity generated by the source of available oxygen and any alkaline compounds present in the wash solution. Said system comprises anhydrous acidifying agent, or mixtures thereof, which needs to be incorporated in the product in an anhydrous form, and to have a good stability in oxidizing environment. Suitable anhydrous acidifying agents for use herein are carboxylic acids such as citric acid, adipic acid, glutaric acid, 3 chetoglutaric acid, citramalic acid, tartaric acid and maleic acid or their salts or mixtures thereof. Other suitable acidifying agents include sodium bicarbonate, sodium sesquicarbonate and silicic acid. Highly preferred acidifying system to be used herein comprise citric acid and/or sodium citrate. Indeed, citric acid can be used in its acidic form or in the form of its salts (mono-, di-, tri- salts) and in all its anhydrous and hydrated forms, or mixtures thereof. It may additionally act as a builder and a chelant, and it is biodegradable. The compositions according to the present invention comprise from up to 20% by weight of the total composition of anhydrous citric acid, preferably from 5% to 15%, most preferably about 10%.

The compositions herein may comprise an alkali metal salt of silicate, or mixtures thereof, amongst the preferred optional ingredients. Preferred alkali metal salt of silicate to be used herein is sodium silicate. In the preferred embodiment herein wherein the soaking compositions comprise an oxygen bleach, it has been found that the decomposition of available oxygen produced in the soaking liquors upon dissolution of the soaking compositions is reduced by the presence of at least 40 parts per million of sodium silicate in said soaking liquors.

Any type of alkali metal salt of silicate can be used herein, including the crystalline forms as well as the amorphous forms of said alkali metal salt of silicate or mixtures thereof.

Suitable crystalline forms of sodium silicate to be used are the crystalline layered silicates of the granular formula

$$NaMSi_xO_{2x+1}\cdot yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20, or mixtures thereof. Crystalline layered sodium silicates of this type are disclosed in EP-A-164 514 and methods for their preparation are disclosed in DE-A-34 17 649 and DE-A-37 42 043. For the purposes of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the a , b , g and d forms of $Na_2Si_2O_5$. These materials are available from Hoechst AG FRG as respectively NaSKS-5, NaSKS-7, NaSKS-11 and NaSKS-6. The most preferred material is d - $Na_2Si_2O_5$, NaSKS-6. Crystalline layered silicates are incorporated in soaking compositions herein, either as dry mixed solids, or as solid components of agglomerates with other components.

Suitable amorphous forms of sodium silicate to be used herein have the following general formula:

$$NaMSi_xO_{2x+1}$$

wherein M is sodium or hydrogen and x is a number from 1.9 to 4, or mixtures thereof. Preferred to be used herein are the amorphous forms of $Si_2O_5$ $Na_2O$.

Suitable Zeolites for use herein are aluminosilicates including those having the empirical formula:

Mz(zAlO2.ySiO2)

wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2; and y is 1; this material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO3 hardness per gram of anhydrous aluminosilicate. Preferred zeolites which have the formula:

Nazí(AlO2)z (SiO2)yù.xH2O

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

Na12í(AlO2)12(SiO2)12ù.xH2O

wherein x is from 20 to 30, especially about 27. This material is known as Zeolite A. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Typically, the compositions herein may comprise from 0.5% to 15% by weight of the total composition of an alkali metal salt of silicate or mixtures thereof, preferably from 1% to 10% and more preferably from 2% to 7%.

The composition herein may also comprise a builder amongst the preferred optional ingredients. All builders known to those skilled in the art may be used herein. Suitable phosphate builders for use herein include sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Other phosphorus builder compounds are disclosed in U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference.

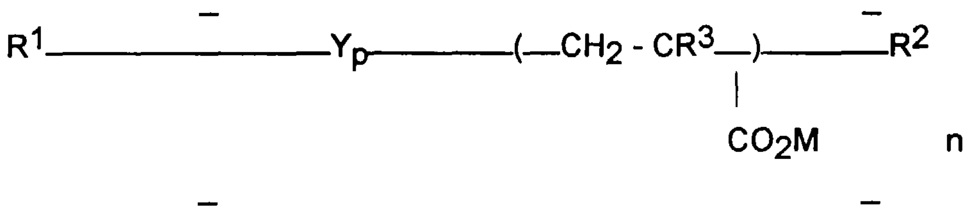
Suitable polycarboxylate builders for use herein include ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, 1,3,5-trihydroxy benzene-2,4,6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the $C_5$-$C_{20}$ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylate builders are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Other suitable polycarboxylate buiders for use herein include builders according to formula I



$$R^1 - \left[ Y_p - \left( CH_2 - \underset{\substack{| \\ CO_2M}}{CR^3} \right) \right]_n - R^2 \qquad \mathrm{I}$$

wherein Y is a comonomer or comonomer mixture; $R^1$ and $R^2$ are bleach- and alkali-stable polymer-end groups; $R^3$ is H, OH or $C_{1-4}$ alkyl; M is H, alkali metal, alkaline earth metal, ammonium or substituted ammonium; p is from 0 to 2; and n is at least 10, or mixtures thereof.

Preferred polymers for use herein fall into two categories. The first category belongs to the class of copolymeric polymers which are formed from an unsaturated polycarboxylic acid such as maleic acid, citraconic acid, itaconic acid, mesaconic acid and salts thereof as first monomer, and an unsaturated monocarboxylic acid such as acrylic acid or an alpha -$C_{1-4}$ alkyl acrylic acid as second monomer. Referring to formula I hereinabove, the polymers belonging to said first class are those where p is not 0 and Y is selected from the acids listed hereinabove. Preferred polymers of this class are those according to formula I hereinabove, where Y is maleic acid. Also, in a preferred embodiment, $R^3$ and M are H, and n is such that the polymers have a molecular weight of from 1000 to 400 000 atomic mass units.

The second category of preferred polymers for use herein belongs to the class of polymers in which, referring to formula I hereinabove, p is 0 and $R^3$ is H or $C_{1-4}$ alkyl. In a preferred embodiment n is such that the polymers have a molecular weight of from 1000 to 400 000 atomic mass units. In a highly preferred embodiment, $R^3$ and M are H.

The alkali-stable polymer end groups $R^1$ and $R^2$ in formula I hereinabove suitably include alkyl groups, oxyalkyl groups and alkyl carboxylic acid groups and salts and esters thereof.

In the above, n, the degree of polymerization of the polymer can be determined from the weight average polymer molecular weight by dividing the latter by the average monomer molecular weight. Thus, for a maleic-acrylic copolymer having a weight average molecular weight of 15,500 and comprising 30 mole % of maleic acid derived units, n is 182 (i.e. 15,500 / (116 x 0.3 + 72 x 0.7)).

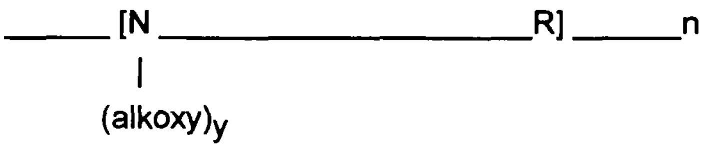
Temperature-controlled columns at 40°C against sodium polystyrene sulphonate polymer standards, available from Polymer Laboratories Ltd., Shropshire, UK, the polymer standards being 0.15M sodium dihydrogen phosphate and 0.02M tetramethyl ammonium hydroxide at pH 7.0 in 80/20 water/acetonitrile.

Of all the above, highly preferred polymers for use herein are those of the first category in which n averages from 100 to 800, preferably from 120 to 400.

Preferred builders for use herein are polymers of maleic or acrylic acid, or copolymers of maleic and acrylic acid.

Typically, the compositions of the present invention comprise up to 50% by weight of the total composition of a builder or mixtures thereof, preferably from 0.1% to 20% and more preferably from 0.5% to 10%.

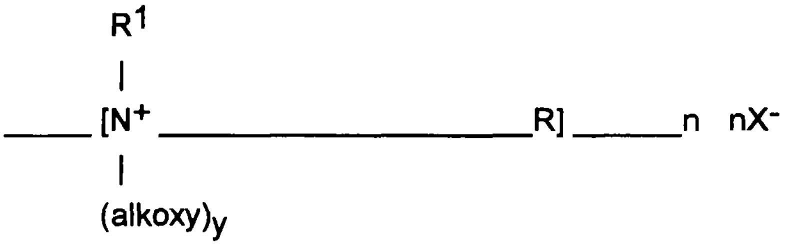
The compositions according to the present invention may further comprise a soil suspending polyamine polymer or mixtures thereof, as optional ingredient. Any soil suspending polyamine polymer known to those skilled in the art may also be used herein. Particularly suitable polyamine polymers for use herein are polyalkoxylated polyamines. Such materials can conveniently be represented as molecules of the empirical structures with repeating units :



$$-[\underset{(\text{alkoxy})_y}{\overset{}{\underset{|}{N}}}-R]-n$$

Amine form

and

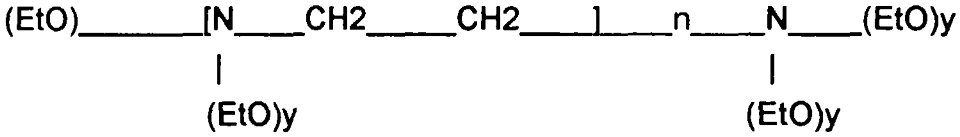


$$-[\underset{(\text{alkoxy})_y}{\underset{|}{\overset{R^1}{\overset{|}{N^+}}}}-R]-n \quad nX^-$$

Quaternized form

wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms; $R^1$ may be a $C_1$-$C_{20}$ hydrocarbon; the alkoxy groups are ethoxy, propoxy, and the like, and y is 2-30, most preferably from 10-20; n is an integer of at least 2, preferably from 2-20, most preferably 3-5; and $X^-$ is an anion such as halide or methylsulfate, resulting from the quaternization reaction.

The most highly preferred polyamines for use herein are the so-called ethoxylated polyethylene amines, i.e., the polymerized reaction product of ethylene oxide with ethyleneimine, having the general formula :



$$(EtO)-[\underset{(EtO)y}{\underset{|}{N}}-CH2-CH2-]-n-\underset{(EtO)y}{\underset{|}{N}}-(EtO)y$$

when y = 2-30. Particularly preferred for use herein is an ethoxylated polyethylene amine, in particular ethoxylated tetraethylenepentamine, and quaternized ethoxylated hexamethylene diamine.

It has surprisingly been found that said soil suspending polyamine polymers contribute to the benefits of the present invention, i.e., that when added in a soaking composition comprising sorbitan ester and a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent, they further improve the stain removal performance of said composition. Indeed, they allow to improve the stain removal performance on a variety of stains including particulate soils, enzymatic stains as well as greasy stains and/or bleachable stains.

Typically, the compositions of the present invention comprise up to 10% by weight of the total composition of such a soil suspending polyamine polymer or mixtures thereof, preferably from 0.1% to 5% and more preferably from 0.3% to 2%.

When the soaking compositions herein comprise an oxygen bleach, it may be desirable for them to further comprise chelating agents which help to control the level of free heavy metal ions in the soaking liquors, thus avoiding rapid decomposition of the oxygen released by said source of available oxygen. Suitable amino carboxylate cheating agents which may be used herein include diethylene triamino pentacetic acid, ethylenediamine tetraacetates (EDTA), N-hydroxyethylethylenediamine triacetates, nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetraamine hexaacetates, and ethanoldiglycines, alkali metal ammonium and substituted ammonium salts thereof or mixtures thereof. Further suitable chelating agents include ethylenediamine-N,N'-disuccinic acids (EDDS) or alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof. Particularly suitable EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof. Also other suitable chelating agents may be the organic phosphonates, including amino alkylene poly(alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or in the form of their metal alkali salt. Preferably the organic phosphonate compounds where present are in the form of their magnesium salt.

The soaking compositions in the present invention may accordingly comprise from 0% to 5% by weight of the total compositions of said chelating agents, preferably from 0% to 3%, more preferably from 0.05% to 2%.

The compositions herein may further comprise a filler like inorganic filler salts such as alkali metal carbonates, bicarbonates and sulphates. Such fillers, for instance sodium bicarbonate, may also act as acidifying agent as described hereinbefore. Accordingly, sodium bicarbonate and sodium sulphate are the preferred filler materials for use herein.

Typically, the compositions of the present invention comprise up to 50% by weight of the total composition of a filler or mixtures thereof, preferably from 0.1% to 15 % and more preferably from 1% to 6%.

Soaking compositions in the present invention may further comprise other optional ingredients such as surfactants, optical brighteners, enzymes, other chelants, dispersants, soil release agents, photoactivated bleaches such as Zn phthalocyanine sulphonate, dyes, dye transfer inhibitors, pigments, perfumes and the like. Said optional ingredients can be added in varying amounts as desired.

The compositions herein can be manufactured in solid, preferably granular, or even in liquid form.

## *B - The process:*

The present invention encompasses processes of soaking fabrics. Indeed, the present invention encompasses a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition as described hereinbefore, for an effective period of time, then removed from said soaking liquor.

As used herein, the expression "process of soaking fabrics" refers to the action of leaving fabrics to soak in a soaking liquor comprising water and a composition as described hereinabove, for a period of time sufficient to clean said fabrics. In contrast to typical laundering operation using a washing machine, the soaking process herein allows prolonged contact time between the fabrics and the soaking liquor, typically up to 24 hours. The soaking process can be performed independently from any other process, such as a typical laundering operation, or a first step before a second, typical laundering step. In the preferred soaking processes of the invention, fabrics are left to soak for a period of time ranging from 10 minutes to 24 hours, preferably from 30 min to 24 hours, more preferably more than 1 hour to 24 hours, even more preferable 2 hours to 24 hours, and most preferably 4 hours to 24 hours. After the fabrics have been immersed in said soaking liquor for a sufficient period of time, they can be removed and rinsed with water. The fabrics can also be washed in a normal laundering operation after they have been soaked, with or without having been rinsed in between the soaking operation and the subsequent laundering operation.

In the soaking process herein, a soaking composition described hereinabove is diluted in an appropriate amount of water to produce a soaking liquor. Suitable doses may range from 45 to 50 grams of soaking composition in 3.5 to 5 liters of water, down to 90 to 100 grams of soaking composition in 20 to 45 liters of water. Typically one dose is 45-50 grams in 3.5 to 5 liters for a concentrated soak (bucket/sink). For washing machine soaked, the dose is 90-100 grams in about 20 (Europe) to 45 (US) liters of water. The fabrics to be soaked are then immersed in the soaking liquor for an appropriate period of time. There are factors which may influence overall performance of the process on particulate dirt/soils. Such factors include prolonged soaking time. Indeed, the longer fabrics are soaked, the better the end results. Ideally, soaking time is overnight, i.e., 8 hours up to 24 hours, preferably 12 hours to 24 hours. Another factor is the initial warm or warmluke temperature. Indeed, higher initial temperatures of the soaking liquors ensure large benefits in performance.

The process herein is suitable for cleaning a variety of fabrics, but finds a preferred application in the soaking of socks, which are particularly exposed to silt and clay pick-up.

In its broadest embodiment the present invention also encompasses a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition comprising a dianionic cleaning agent, as defined herein, and/or an alkoxylated dianionic cleaning agent, as defined herein, for more than 1 hour, preferably more than 2 hours and more preferably 4 hours to 24 hours, then removed from said soaking liquor. Indeed, it has been found that when adding such a dianionic cleaning agent and/or an alkoxylated dianionic cleaning agent, in a soaking composition, improved particulate soil removal and/or improved enzymatic stain removal is obtained.

## The stain removal performance test method:

The stain removal performance of a given composition on a soiled fabric under soaking conditions, may be evaluated by the following test method. Soaking liquors are formed by diluting for instance 45 g of the soaking compositions herein in 3.78 liters of water or 90 g of the soaking composition in 45 liters of water. Fabrics are then immersed in the resulting soaking liquor for a time ranging from 30 minutes to 18 hours. Finally, the fabrics are removed from the soaking liquors, rinsed with water and washed with a regular washing process, handwash or washing machine wash, with a regular detergent, with or without re-using the soaking liquor, then said fabrics are left to dry.

For example, typical soiled fabrics to be used in this stain removal performance test may be commercially available from EMC (Empirical Manufacturing Company) Cincinnati, Ohio, USA, such as clay, grass, spaghetti sauce, gravy, dirty motor oil, make-up, barbecue sauce, tea, blood on two different substrates: cotton (CW120) and polycotton (PCW28).

The stain removal performance may be evaluated by comparing side by side the soiled fabrics pretreated with the composition according to the present invention with those pretreated with the reference, e.g., the same composition without such a dianionic cleaning agent or alkoxylated dianionic cleaning agent according to the present invention. A visual grading scale may be used to assign differences in panel score units (psu), in a range from 0 to 4.

The following examples will further illustrate the present invention.

## Examples

The following compositions are prepared by mixing the listed ingredients in the listed proportions.

| Ingredients | 1 (%w/w) | 2 (%w/w) | 3 (%w/w) |
|---|---|---|---|
| Sorbitan mono-stearate (SMS) | 0.5 | 0.5 | 0.5 |
| Citric acid | 11 | 11 | 11 |
| NOBS | 12 | 12 | 12 |
| Polyacrylate (Acusol 445ND) | 11 | 11 | 11 |
| Sodium percarbonate | 31 | 31 | 31 |
| 2-dodecyl 1,4- butane disulphate | 0.7 | - | - |
| 2-hexadecyl 1,4 butane disulphate | - | 0.7 | - |
| 2-octadecyl 1,4 butane disulphate | - | - | 0.7 |
| Anionic (LAS/AS/AES) | 8 | 8 | 8 |
| DTPA | 0.2 | 0.2 | 0.2 |
| Others, Inerts and minors | up to 100 | up to 100 | up to 100 |

| Ingredients | 4 (%w/w) | 5 (%w/w) | 6 (%w/w) |
|---|---|---|---|
| Sorbitan mono-stearate (SMS) | 0.5 | 0.5 | 0.5 |
| Citric acid | 11 | 11 | 11 |
| NOBS | 12 | 12 | 12 |
| Polyacrylate (Acusol 445ND) | 11 | 11 | 11 |
| Sodium percarbonate | 31 | 31 | 31 |
| 2-C14 1,4- butane disulphate | 0.7 | - | - |
| 2-decyl 1,4 butane disulphate | - | 0.7 | - |
| 2-octyl 1,4 butane disulphate | - | - | 0.7 |
| Anionic (LAS/AS/AES) | 8 | 8 | 8 |
| DTPA | 0.2 | 0.2 | 0.2 |
| Others, inerts and minors | up to 100 | up to 100 | up to 100 |

| **Ingredients** | **7** (%w/w) | **8** (%w/w) | **9** (%w/w) |
|---|---|---|---|
| Sorbitan mono-stearate (SMS) | 2.50 | 0 | 0 |
| Sorbitan monostearate EO 20 (SMS EO 20) | 0 | 3.00 | 0 |
| Sorbitan tristearate EO 20 (STS EO 20) | 0.50 | 0 | 3.00 |
| Citric acid | 10 | 10 | 10 |
| Blend of 1,4-disulphates (C18-C22) | 1 | 1 | 1 |
| Polyacrylate (Acusol 445 ND) | 11 | 11 | 11 |
| Silicate (amorphous; 1.6r) | 0.4 | 0.4 | 0.4 |
| Sodium perborate monohydrate | 0 | 0 | 0 |
| Sodium percarbonate | 31 | 31 | 31 |
| Sodium sulphate | 24 | 24 | 24 |
| NOBS | 6 | 6 | 6 |
| TAED | 5 | 5 | 5 |
| Anionic (LAS/AS/AES) | 7 | 7 | 7 |
| Others, inerts and minors | up to 100 | up to 100 | up to 100 |

| **Ingredients** | **10** (%w/w) | **11** (%w/w) | **12** (%w/w) |
|---|---|---|---|
| Sorbitan mono-stearate (SMS) | 0.5 | 0.5 | 0.5 |
| Citric acid | 11 | 11 | 11 |
| NOBS | 12 | 12 | 12 |
| Polyacrylate (Acusol 445ND) | 11 | 11 | 11 |
| Sodium percarbonate | 31 | 31 | 31 |
| C16 alkyl 1,4 ethoxylated disulphate | 2.0 | 0 | 0 |
| C14 alkyl 1,4 ethoxylated disulphate | 0 | 2.0 | 0 |
| C18 alkyl 1,4 ethoxylated disulphate | 0 | 0 | 2.0 |
| Anionic (LAS/AS/AES) | 8 | 8 | 8 |
| DTPA | 0.2 | 0.2 | 0.2 |
| Others, inerts and minors | up to 100 | up to 100 | up to 100 |

Soaking liquors are formed by diluting 45 g of each of the above compositions 1 to 12 in between 3.5 lit. to 5.0 lit. of water. 0.5 to 2 Kg of fabrics are then each time immersed in said soaking liquors for a time ranging from 10 minutes to 24 hours. Finally, the fabrics are removed from the soaking liquors, rinsed with water and washed with a regular washing process, handwash or washing machine wash, with a regular detergent, with or without re-using the soaking liquor, then said fabrics are left to dry. Excellent stain removal performance is obtained with these compositions on various stains including mud/clay stains, enzymatic stains, greasy stains, bleachable stains and the like.

| Ingredients | 13 (%w/w) | 14 (%w/w) | 15 (%w/w) |
|---|---|---|---|
| Citric acid | 11 | 11 | 11 |
| NOBS | 12 | 12 | 12 |
| Polyacrylate (Acusol 445ND) | 11 | 11 | 11 |
| Sodium percarbonate | 31 | 31 | 31 |
| 2-C14 1,4- butane disulphate | 0.7 | - | - |
| 2-decyl 1,4 butane disulphate | - | 0.7 | - |
| 2-octyl 1,4 butane disulphate | - | - | 0.7 |
| Anionic (LAS/AS/AES) | 8 | 8 | 8 |
| DTPA | 0.2 | 0.2 | 0.2 |
| Others, inerts and minors | up to 100 | up to 100 | up to 100 |

Soaking liquors are formed by diluting 45 g of each of the above compositions 13 to 15 in between 3.5 lit. to 5.0 lit. of water. 0.5 to 2 Kg of fabrics are then each time immersed in said soaking liquors for more than 1 hour, typically 4 hours to 24 hours. Finally, the fabrics are removed from the soaking liquors, rinsed with water and washed with a regular washing process, handwash or washing machine wash, with a regular detergent, with or without re-using the soaking liquor, then said fabrics are left to dry. Good stain removal performance is obtained with these processes on various stains including mud/clay stains, enzymatic stains, greasy stains, bleachable stains and the like.

## Claims

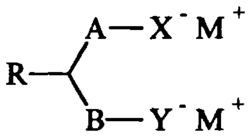
1. A soaking composition comprising:

   - a sorbitan ester according to the formula $C_6H_9O_2$ $(C_2H_4O)_x$ $R_1R_2R_3$, wherein x is an integer of from 0 to 40, $R_1$, $R_2$ are independently OH or $(C_n H_{n+1})COO$, and $R_3$ is $(C_n H_{n+1})COO$ group, where n is an integer of from 11 to 17; and

   - a dianionic cleaning agent comprising a structural skeleton of at least five carbon atoms to which two anionic substituent groups spaced at least three atoms apart are attached, wherein one anionic substituent group is a sulfate group and the other anionic substituent is selected from sulfate and sulfonate, and/or

   - an alkoxylated dianionic cleaning agent comprising a structural skeleton of at least five carbon atoms to which two anionic substituent groups spaced at least three atoms apart are attached, wherein one anionic substituent group is an alkoxy-linked sulfate group and the other anionic substituent is selected from sulfate and sulfonate, optionally alkoxy-linked.

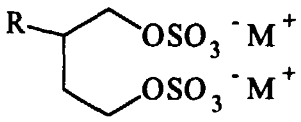
2. A composition according to claim 1 wherein said dianionic cleaning agent has the formula



where R is an alkyl, substituted alkyl, alkenyl, aryl, alkaryl, ether, ester, amine or amide group of chain length $C_1$ to $C_{28}$, or hydrogen; A and B are independently selected from alkyl, substituted alkyl, and alkenyl groups of chain length $C_1$ to $C_{28}$, or a covalent bond, and A and B in total contain at least 2 atoms; A, B, and R in total contain from 4 to 31 carbon atoms; X and Y are anionic groups selected from the group consisting of sulfate and sulfonate, provided that at least one of X or Y is a sulfate group; and M is a cationic moiety.

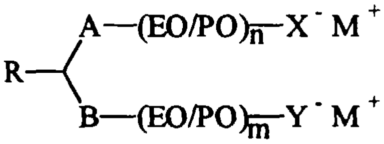
3. A composition according to claim 2 wherein the anionic substituent groups are substituted at a 1-4 position on the structural skeleton.

4. A composition according to any of the preceding claims wherein said dianionic cleaning agent has the formula:



wherein R is a straight or branched chain alkyl or alkenyl group of chain length from $C_4$ to $C_{18}$; and M is a cationic moiety

5. A composition according to any of the preceding claims wherein said alkoxylated dianionic cleaning agent has the formula



where R is an alkyl, substituted alkyl, alkenyl, aryl, alkaryl, ether, ester, amine or amide group of chain length $C_1$ to $C_{28}$, or hydrogen; A and B are independently selected from alkyl, substituted alkyl, and alkenyl group of chain length $C_1$ to $C_{28}$, or a covalent bond; EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein n and m are independently within the range of from 0 to 10, with at least m or n being at least 1; A and B in total contain at least 2 atoms; A, B, and R in total contain from 4 to 31 carbon atoms; X and Y are anionic groups selected from the group consisting of sulfate and sulfonate, provided that at least one of X or Y is a sulfate group; and M is a cationic moiety.

6. A composition according to claim 5 wherein the anionic substituent groups are substituted at a 1-4 position on the structural skeleton

7. A composition according to any of the preceding claims which comprises from 0.01% to 50% by weight of the total composition of said dianionic cleaning agent or mixtures thereof, preferably from 0.05% to 10% and more preferably from 0.1% to 5%, and/or from 0.01% to 50% by weight of the total composition of said alkoxylated dianionic cleaning agent or mixtures thereof, preferably from 0.05% to 10% and more preferably from 0.1% to 5%.

8. A composition according to any of the preceding claims where said sorbitan ester is polyethoxylated (20) sorbitan tristearate, or polyethoxylated (20) sorbitan monostearate, or sorbitan monostearate, or sorbitan monopalmitate, or mixtures thereof.

9. A composition according to any of the preceding claims which comprises a non-ethoxylated sorbitan ester and an ethoxylated sorbitan ester.

10. A composition according to any of the preceding claims which comprises from 0.01% to 10% of said sorbitan ester or mixtures thereof, preferably from 0.01% to 5%, and more preferably from 0.5% to 5%.

11. A composition according to any of the preceding claims which further comprises at least one optional ingredient selected from the group consisting of acidifying agents, alkali metal salt of silicate, builders, soils suspending polyamine polymers, fillers, surfactants, optical brighteners, enzymes, chelating agents, dispersants, soil release agents, dyes, dye transfer inhibitors, pigments, perfumes and mixtures thereof.

12. A composition according to any of the preceding claims which further comprises an oxygen bleach at a level of from 0.01% to 80% by weight of the total composition, preferably from 5% to 45% and more preferably from 10% to 40%.

**13.** A composition according to claim 12 which comprises an activator for said bleach up to a level of 30% by weight of the total composition.

**14.** A process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition according to any of the preceding claims, for an effective period of time, then removed from said soaking liquor.

**15.** A process according to claim 14 wherein said time ranges from 10 minutes to 24 hours, preferably 30 minutes to 24 hours, more preferably more than 1 hour up to 24 hours and most preferably 4 hours to 24 hours.

**16.** A process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition comprising a dianionic cleaning agent comprising a structural skeleton of at least five carbon atoms to which two anionic substituent groups spaced at least three atoms apart are attached, wherein one anionic substituent group is a sulfate group and the other anionic substituent is selected from sulfate and sulfonate, and/or an alkoxylated dianionic cleaning agent comprising a structural skeleton of at least five carbon atoms to which two anionic substituent groups spaced at least three atoms apart are attached, wherein one anionic substituent group is an alkoxy-linked sulfate group and the other anionic substituent is selected from sulfate and sulfonate, optionally alkoxy-linked, for more than 1 hour, preferably more than 2 hours and more preferably 4 hours to 24 hours, then removed from said soaking liquor.

European Patent
Office

# EUROPEAN SEARCH REPORT

Application Number
EP 96 87 0123

## 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.6) |
|---|---|---|---|
| A | FR 2 289 606 A (PROCTER & GAMBLE)<br>* page 13, line 20 - line 40 *<br>* page 18, line 19 - line 22 *<br>--- | 1,8-16 | C11D1/83<br>C11D1/66 |
| A | WO 96 09761 A (DIVERSEY CORP ET AL.)<br>* claims *<br>--- | 1,8-16 | |
| A | GB 1 540 301 A (JOHNSON & JOHNSON)<br>* claims *<br>--- | 1 | |
| A | WO 96 07473 A (HENKEL KGAA )<br>* claims *<br>--- | 1 | |
| A | US 3 850 854 A (WEIL I)<br>* claims *<br>--- | 1,2 | |
| A | EP 0 590 521 A (TOMEI SANGYO KK)<br>* claims *<br>----- | 1 | |

**TECHNICAL FIELDS SEARCHED (Int.Cl.6)**

C11D

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| BERLIN | 7 February 1997 | Pelli Wablat, B |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

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E : earlier patent document, but published on, or after the filing date
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