A structured aqueous liquid detergent composition comprising: at least 10 wt% water, at least 0.5 wt% surfactant, at least 0.0001 wt% of enzyme selected from lipase, cellulase and mixtures thereof, an external structurant, characterised in that the external structurant comprises at least 0.15 wt%, preferably at least 0.2%, citrus fibre that has been mechanically pulped and swollen in water.
EXTERNALLY STRUCTURED AQUEOUS DETERGENT LIQUID

Technical Field

This invention relates to a structured aqueous detergent liquid composition comprising water, surfactant, external structurant and enzymes, the external structurant provides rheological modification to the composition and may also be used to suspend solid materials in the liquid.

Background

It is desirable to formulate liquid detergents in a concentrated form. This saves on packaging, transport costs and production energy. In WO09153184, a concentrated aqueous laundry detergent liquid is used to reduce the amount of chemicals per wash. This is achieved, without loss of detergency, by reduction of the amount of surfactant used per wash and use, in its place, of highly weight efficient enzymes and polymers to boost detergency on everyday dirt and stains. Preferred compositions use lipase enzyme and/or combinations of high levels of ethoxylated polyethyleneimine polymer and polyester soil release polymer.

It is known to use external structurants in aqueous detergent liquids for rheological modification and suspending duty. For a concentrated liquid, the structurant can convey the idea of concentration by increasing low shear viscosity whilst allowing the composition to flow freely when poured. Solid materials can be suspended in such liquids to further reinforce the concentration message, for example the liquid can be pearlised by inclusion if mica particles or titanium dioxide particles. The external structurant should be capable of suspending these particles, working either alone, or in combination with another rheology modifying system.
External structurants are also useful for less concentrated aqueous cleaning liquids. In such liquids, surfactant in excess of that required for detergency is often used for thickening and rheology modification. This is undesirable from an environmental standpoint, not only is more chemical sent to waste but frequently the excess surfactant causes the utilisation of more rinse water, which is a big issue when water is a scarce resource.

One well-known external structurant is hydrogenated castor oil (HCO), also known as trihydroxystearin, or castor wax, and sold under the trade name Thixcin® by Elementis. HCO is derived from chemical modification of a plant extract. Then the HCO is converted into an external structurant by crystallising it in the liquid, or in part of the liquid. This crystallisation process may impose formulation constraints, especially when using high surfactant levels. HCO structured liquids are slightly cloudy, which is undesirable when visual cues are suspended in the liquid. We have found that HCO is liable to rapid decomposition in the presence of lipase enzyme. Thus, the desirable use of this enzyme, particularly for the use disclosed in WO091 531 84 has been found to be incompatible with this typical external structurant.

US2009/02 17463 A1 discloses, in Examples C (A-E), externally structured liquid detergent compositions comprising HCO and lipase enzymes. The HCO external structurant would lose its ability to suspend, and have its rheology modifying properties adversely affected, in a few hours when formulated in a detergent liquid comprising lipase enzyme, as described in US2009/021 7463.

It has been proposed to use bacterially produced microfibrous cellulose (MFC) as an external structurant, either on its own (US2007/01 97779), or more preferably in combination with HCO, as described in WO201 0/0481 54. Compared with HCO, MFC is more weight efficient as an external structurant. Furthermore it is not based on oily substances, so should not suffer from lipase enzyme attack.
However, MFC suffers from other disadvantages. The first is that due to its very low incorporation levels it can fail to remain evenly dispersed through the liquid if air micro bubbles form and get trapped by the structuring network to buoy the MFC up. A process designed to try to overcome this problem is disclosed in WO09135765A (Unilever). No enzymes are used. The detergent formulator would prefer to avoid use of MFC due to these known processing constraints.

US patent application US2007/01 97779 discloses a structurant consisting of bacterially produced MFC combined with significant levels of carboxy methylcellulose and xanthan gum as dispersion aids. Upon high shear dispersion in water, the MFC forms a 3-D network structure, which can suspend inert materials such as sand and nylon beads. The xanthan gum part of the dispersant is not a desirable ingredient for many detergent liquids. It poses constraints for inclusion of enzymes that can decompose xanthan gum. Furthermore it can have an undesirable effect in combination with cleaning and soil release polymers. Such polymers are proposed to be used at high concentrations in the detergent liquids described in WO09/153184. Thus MFC is not a good choice for the external structuring of such detergent liquids with high levels of polymers.

WO2009/101545 describes compositions comprising MFC structurant. Exemplary compositions contain enzymes; a list of suitable enzymes is given on page 29. The preferred enzyme mixture includes cellulase. We have determined that use of some cellulases with MFC reduce its suspending power and adversely affect the rheological modification imparted by the MFC. We have also discovered that MFC requires the presence of relatively high levels of surfactant to provide effective rheological modification. It would be desirable to find an alternative external structurant that would also perform at low surfactant levels and that would be compatible with a wide range of cellulase enzymes.
Based on SEM evidence, MFC forms nanofibres in concentrated aqueous detergent liquids. Uncertainties exist in scientific understanding of the impacts of such fibres, and associated public perception. For this reason, and because of the other disadvantages of MFC outlined previously, the skilled worker desires to find a better substitute for the lipase vulnerable HCO than MFC appears to be.

Especially in the laundry detergent field it is normal to provide a range of products with a common chassis. Some of those products will comprise enzymes and others may be the so-called non-bio variants that are free from enzymes to allow use by consumers who prefer not to contact their laundry with enzyme containing formulations. It adds considerably to formulation complexity if the external structurant cannot be used in a common composition chassis designed to work both with and without the enzyme system adopted. It is thus highly desirable to have a chassis with a rheology modified by an external structurant that can be used with lipase and/or cellulase or no enzyme at all and in which solid material can be reliably and stably suspended. Thus, it would be beneficial in the field of externally structured aqueous detergent compositions to have a new external structurant that does not sufferer from the drawbacks of HCO and/or MFC.

US2004/0086626 describes an improved method for refining cellulose that produces a highly refined cellulosic (HRC) material. The method comprises soaking raw material from primarily parenchymal cell wall structures in an aqueous solution, using reduced temperatures and pressures, and refining the material with a plate refiner. After drying the resulting HRC fibre displays a water retention capacity of about 25 to at least about 56 g water/g dry HRC and retains moisture under conditions that are ordinarily used to remove moisture from materials. The publication suggests that the HRC fibre product can also provide excellent thickening properties and may be used in a wide variety of materials, including edible materials. Thickening and suspending properties are particularly attributed to fibres provided by sugar beets. Orange pulps are used in several
examples. The main use envisaged for this product is as a food additive. The dried HRC product may be rehydrated by the use of a high shear mixer to disperse organic fibre plant mass materials rapidly into solution. Other uses mentioned are industrial thickeners, as in paint thickeners, stain thickeners, coating thickeners, and the like.

High water binding capacity Citrus fibres are available for example as "Herbacel AQ plus citrus fibre", from Herba Foods.

Summary of the Invention

According to the present invention there is provided a structured aqueous liquid detergent composition comprising:

at least 10 wt% water,

at least 0.5 wt% surfactant,

at least 0.0001 wt% of enzyme selected from lipase, cellulase and mixtures thereof.

an external structurant,

characterised in that the external structurant comprises at least 0.15 wt%, preferably at least 0.2%, citrus fibre that has been mechanically pulped and swollen in water.

Preferably the composition comprises 0.16 to 0.35 wt% pulped citrus fibre.

The composition may have a yield stress greater than 0.2 Pa.

Citrus fibre is derived from citrus fruit; advantageously it comprises the peel of lemons and/or limes. The citrus fruit peel is pulped by subjecting it to high shear and the pulped material is referred to as pulped citrus fibre. Such pulped fibres are capable of absorbing and binding at least 15 times its own weight of water, preferably at least 20 times and even up to 30 times.
The minimum amount of pulped citrus fibre required to deliver an acceptably high critical stress in the final liquid is 0.15 wt%.

The composition comprises at least one enzyme selected from lipase and cellulase. The preferred amount of each enzyme is from 0.0001 to 5 wt%, even more preferably from 0.001 to 0.3 wt% active enzyme. The preferred enzyme is lipase.

The external structurant is a pulped citrus fibre which has undergone a mechanical treatment comprising a step of high intensity mixing in water and which material has consequently absorbed at least 15 times its own dry weight of water, preferably at least 20 times its own weight, in order to swell it. It may be derived by an environmentally friendly process from a fruit processing waste stream. This makes it more sustainable than prior art external structurants.

Furthermore, it requires no additional chemicals to aid its dispersal and it can be made as a structured premix to allow process flexibility.

Pulped citrus fibre is much less expensive to produce than bacterial cellulose because its processing is simpler and it may be made from a waste stream, e.g. from fruit juice production.

Citrus fruits are preferred as the source of the fibre because they have a large amount of peel that can provide material with the desired water absorbing capacity. The most preferred fruits are lemons and limes lemon because the natural pH of the resulting mechanical pulp is about 3.5, which allows use of potassium sorbate at low levels as an effective preservative for the premix before it is dispersed into the detergent liquid.

In a preferred process, the citrus fibre is mechanically pulped by processing it to make a premix preferably in combination with preservative. This is done by
adding dried powdered citrus fibre to at least 15 times its own weight of water and dispersing it under very high shear to further break up the citrus fibres and to begin the process of hydration, or swelling. The mechanically treated citrus fibre is left in contact with the water for sufficient time for it to swell due it being fully hydrated. This can be several hours. We have found it advantageous that pulped citrus fibre is kept separate from surfactant until it is fully swollen. This avoids the possibility for the surfactant to compete with the citrus pulp fibre for the water. Something that becomes more of a problem as the total surfactant concentration increases. This premix pulp swelling process seems to become especially advantageous when surfactant level in the composition is 25 wt% or higher. The very high shear may be provided by a high intensity mixer such as a Silverson mixer, or, less preferably, by means of a High-pressure homogeniser. The homogeniser is less preferred because it can suffer from blockage problems with citrus fibre.

The amount of pulped citrus fibre in the premix is preferably from 1 to 5 wt%. More preferably from 2 to 4 wt%. Depending on the processing equipment used there may be a practical upper limit of from 3.3 to 3.5 wt% as it is advantageous that there is excess water in order to fully hydrate the pulped citrus fibre.

Pulped Citrus fibre has different in use pouring properties from other external structurants used in detergent compositions. It exhibits pronounced drainage on walls of a pack, a translucent appearance, and a slightly grainy texture on pouring. This gives a detergent liquid structured with pulped citrus fibre a different look and feel for the consumer. Such a difference is ideal to signal a major shift in liquid detergent composition; especially to a composition that requires lower usage and a change in consumer behaviour. Unlike some external structurants, notably MFC, pulped citrus fibre does not significantly affect the foam generated by the presence of the surfactant system. This is an advantage for formulation flexibility.
Pulped Citrus fibre is complex and heterogeneous; it includes both soluble and insoluble cellular materials, which is shown to give rise to a distinctive network of 'sponges' of varying size and geometry in contrast to MFC's essentially fibrous network. Possibly due in part to this structural difference, one advantage we have found for pulped citrus fibre externally structured liquid formulations is its compatibility with enzymes. In particular, Lipase, which is found rapidly to degrade an HCO structured liquid and cellulases which appear to have some effect on MFC.

Thus at least one enzyme selected from lipase and cellulase is an essential feature of the detergent compositions of the invention.

Lipase is a preferred enzyme as is known to boost performance on certain types of stains and soil when used in compositions designed to provide low in solution surfactant levels. Among the suitable Lipases are Lipomax®, Lipex®, and Lipolase®. Preferred lipase enzymes include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola*, including ones which comprise a polypeptide having an amino acid sequence which has at least 90% sequence identity with the wild-type lipase derived from *Humicola lanuginosa*, most preferably strain DSM 4109. However, when used at low in wash surfactant levels so-called "multi-wash" lipase enzymes may also show a single-wash benefit. The amount of lipase enzyme protein used in the wash is set to be at the high side of what is normal (>5 mg, preferably greater than 8 mg per wash). This means that the amount in the composition is higher than typically found in liquid detergents. The composition preferably comprises from about 5 to about 20000 LU/g of a lipase. A particularly preferred lipase enzyme has been published under the trademark Lipoclean™ by Novozymes. Lipomax® from Genencor is also preferred.
Cellulases may be included and if they are the formulation should preferably be formulated at a pH where their activity is low. Typically this is an alkaline pH, although mildly acidic conditions of down to pH 6.5 or even as low as pH 6.2 can be tolerated. An advantage of pulped citrus fibre over bacterially derived microfibrous cellulose as an external structurant is that due to its lower cost and lower efficacy as a structurant the pulped citrus fibre is incorporated at much higher levels than MFC. This appears to confer the advantage of greater resistance to destabilisation of the structuring system due to attack from cellulase. Pulped citrus fibre provides a stable external structuring network in the presence of endoglucanase, which enables addition of this cellulase to a structured aqueous liquid either on its own, or more preferably in combination with lipase. Such a mix of enzymes is desirable for compositions that further comprise a soil release polymer to provide a multi wash benefit on a range of stain and fabric types. Concentrated laundry detergent liquids may advantageously contain such a combination. Cellulase improves the cleaning of cotton, lipase improves the cleaning of oily soils from cotton and polyester and soil release polymers further boost the multi-wash cleaning benefits of the detergent composition on these fabrics.

For structured detergent compositions used for cleaning hard surfaces, including hand dishwashing liquids, lipase helps remove greasy stains, especially if low surfactant levels are used. Cellulases help to break down many other food residues.

The surfactant type is not limited. Synthetic detergents are preferred. Mixtures of synthetic anionic and nonionic surfactants, or wholly anionic surfactant system or admixtures of anionic surfactants with nonionic surfactants or with amphoteric or zwitterionic surfactants may be used. It is preferred for the composition to comprise anionic (non-soap) surfactant. Particularly preferred surfactant systems are mixtures of the anionic surfactants linear alkyl benzene sulphonate and
sodium lauryl ether sulphate with the nonionic surfactant ethoxylated nonionic fatty alcohol. Betaines, such as sulphobetaine are advantageously used as a cosurfactant.

The amount of surfactant may range from 0.5 to 65 wt%, preferably 2.5 to 60 wt%, more preferably from 25 to 50 wt%. The skilled worker will appreciate that the optimum surfactant concentration will largely depend on the product type and the intended mode of use.

The amount of external structurant is important. Because it is added to the remainder of the ingredients in admixture with around 20 times its weight of water, it is important to keep the amount of structurant to a minimum. Below 0.15 wt%, pulped citrus fibre fails to provide adequate structuring. The precise lower limit depends to some extent on the remainder of the composition; the skilled worker will know that the aim is to obtain a system in which the rheology exhibits a critical yield stress. To ensure adequate suspending duty it is preferred that the amount of pulped citrus fibre is at least 0.2 wt%. The structured liquid is shear thinning. The preferred pouring viscosity being from 20 - 100 mPa.s and the yield stress or critical stress being about 0.3 Pa.

The composition may optionally comprise suspended solid material. The solid material may be microcapsules such as perfume encapsulates, or care additives in encapsulated form. It may alternatively, or additionally, take the form of insoluble ingredients such as silicones, quaternary ammonium materials, insoluble polymers, insoluble optical brighteners and other known benefit agents found, for example, in EP1328616. The amount of suspended solid material may be from 0.001 to up to 10 or even 20 wt%. A particular solid material to be suspended is a visual cue, for example the type of flat film cue described in EP13119706. The cue may itself contain a segregated component of the composition. Because the cue must be water-soluble, yet insoluble in the composition, it is conveniently
made from a modified polyvinyl alcohol that is insoluble in the presence of anionic surfactant. In that case, the detergent composition should comprise some anionic surfactant, preferably at least 5 wt% anionic surfactant.

According to a second aspect of the invention there is provided a process to manufacture a pulped citrus fibre structured detergent liquid comprising at least 0.15 wt% pulped citrus fibre structurant and at least 0.5 wt% surfactant, the process comprising the steps of:

a) Selecting a citrus fruit material, preferably one with low sugar content, comprising citric acid or citrate,

b) forming citrus fibres from the citrus fruit material, preferably by extraction,

c) subjecting the citrus fibres to mechanical processing comprising application of shear in the presence of at least 15 times the amount of water based on the citrus fibres, the shear being sufficient to cause structural disruption and hydration of the citrus fibres to form a structuring premix comprising dispersed pulped citrus fibre; and

d) further dispersing the pulped citrus fibre structuring premix into a de-aerated detergent liquid to form an externally structured detergent liquid comprising surfactant; and

e) adding enzymes selected from lipase, cellulase and mixtures thereof to the externally structured detergent liquid.

Advantageously the detergent liquid in step (d) contains citrate builder. Preferably, it comprises 1 to 20 wt% hydrotropes. If the liquid is to be clear and the visual distinctiveness of the pulped citrus fibre external structurant is to be utilised fully, it desirably comprises no opacifier or pearliser. It may, however, comprise colorant.

The dispersal requires no addition of further dispersal aids to the premix formed in step (c). Advantageously a preservative is added to the premix during or after
step (c), particularly if the premix will be stored for some time before addition to the detergent liquid.

A further advantage of the use of pulped citrus fibre as an external structurant is that, unlike some other external structurants, it appears not to modify the type or amount of foam formed by a detergent liquid. This is important because it enables the structurant to be added to an aqueous detergent composition without affecting its in use properties. This is particularly the case for compositions that are mixed with a comparatively large volume of water for cleaning use. In this category may be mentioned especially liquid laundry detergent compositions, both concentrated and dilute, contained in both bottle and unit dose formats, for example sachets, and hand dishwashing compositions. Other compositions that are used neat, including laundry liquids used for pre-treatment and hard surface cleaning compositions of the type that are applied from a spray or pump are beneficially structured with this external structurant as it does not cause over foaming as they are applied and very low levels of surfactant can be structured. Furthermore, the structurant is compatible with the inclusion of lipase for grease removal, especially in compositions that may be left on hard surfaces for grease removal purposes and other hard surface cleaning compositions. The externally structured enzyme containing compositions are suitable for hand contact after dilution uses, such as hand dishwashing and hand laundry.

Laundry detergents are generally classified as low foam, used in automatic washing machines, and high foam, used in hand wash and top loading washing machines. The pulped citrus fibre advantageously provides the necessary structuring without boosting foam in the low foaming compositions and yet retains adequate foam in high foaming compositions.
Detailed Description of the Invention

Pulped Citrus fibre
When supplied in the form of a premix the level of pulped citrus fibre in the premix preferably lies in the range 1 to 2.5 wt%. When added to a detergent liquid the amount of pulped citrus fibre preferably lies in the range of 0.15 wt% to 0.35 wt%.

A particularly preferred grade of citrus fibre is supplied under the name "Herbacel AQ plus citrus fibre", ex Herba Foods. This citrus fibre has a total (soluble and insoluble) fibre content of greater than 80% and soluble fibre content of greater than 20%. It is supplied as a fine dried powder with low colour and has a water binding capacity of 20 kg water per kg of powder.

Because the dispersed pulped citrus fibre is biodegradable, it is advantageous to include a preservative into the premix. In any case, a preservative is normally needed in the liquid detergent composition.

The albedo of citrus fruits is the main source of the citrus fruit peel used to make the powdered citrus fibre. It has a 'spongy microstructure'. Citrus fruits (mainly lemons and limes) are dejuiced to leave the insoluble plant cell wall material and some internally contained sugars and pectin. It is dried and sieved and then washed to increase the fibre content. The refining process may entail soaking the fibres in NaOH (<1 %), draining and standing to soften, before shearing, refining and & drying. Dried materials are large (100's micron cell fragment, consisting of tightly bound/bonded fibrils). After drying and milling a powdered citrus fibre material is obtained. The process used leaves much of the natural cell wall intact while the sugars are removed. The resulting highly swelling citrus fibre materials are typically used as food additives and have been used in low fat mayonnaise. The pH of the dispersed powder is acidic which is ideal for use with a preservative such as potassium sorbate.
Microscopy shows that the powdered citrus fibre material as supplied it is a heterogeneous mixture of particles with various sizes and shapes. The majority of the material consists of aggregated lumps of cell walls and cell wall debris. However, a number of tube-like structures with an open diameter of about 10 micron that are often arranged in clusters, can be identified. These, so called, xylem vessels are water transport channels that are mainly located in the peel of citrus fruits. The xylem vessels consists of stacks of dead cells, joined together to form long tubes, 200 to 300 micron long. The outside of the tubes is reinforced by lignin, which is often laid down in rings or helices preventing the tubes from collapse due to the capillary forces acting on the tube walls during water transport. The citrus fibre as supplied does not contain polymeric or other dispersants that are commonly found at high levels in other external structurants including MFC. For example, CP Kelco MFC is a combination of fibre (60%) with other swelling polymers (40%), such as xanthan, to make it easier to disperse. For applications where skin is exposed to the liquid, for instance hand dish wash compositions, the absence of such polymers may avoid negative sensorial attributes such as sliminess or stickiness. The absence of any additional polymers or gums ensures the required rheology of the pulped citrus fibre as an external structurant. It also makes this external structurant highly compatible with other polymers or thickeners that may be included into the composition. Especially soil release polymers, for example those designed to release dirt from polyester fabrics, and cleaning polymers, for example ethoxylated polyethylene imines, especially PEI 600 20 EO (EPEI): a polyethylene imine with a Mwt of the polymer backbone of approximately 600 and an average of 20 moles of ethylene oxide for each Nitrogen.

Before it can be used as an external structurant it is necessary to process the powdered citrus fibre material as supplied further to break down the tubes to be more space filling. This is done by dispersing it at a low concentration into water. As mentioned previously a preservative is usefully added at this stage. This high
shear dispersal opens out the sponge structure to increase the phase volume. The shear should not be high enough to lead to defibrillation. If a high-pressure homogeniser is used it should be operated between 200 and 600 bar. The more shear that is applied the less dense the resulting particles. Whilst the morphology is changed by the high shear, process aggregate size appears not to be changed.

At high pressure, the fibres break down and then fill the water phase. The very high shear also forms fibrils by rubbing loose the outer parts of the cell walls and these are able to form a matrix that structures the water outside of the volume of the original fibre.

A pulped citrus fibre structuring premix may alternatively be made using a high shear mixer, such as a Silverson. One possible process passes the premix through several sequential high-shear mixing stages in order to ensure full hydration and dispersal of the citrus fibre to form the pulped citrus fibre dispersion.

The premix can then simply be added to a partially, or formed detergent liquid premix with the surfactant and other components of the liquid detergent composition already admixed. Ingredients that would be held back at this stage are perfume, enzymes and any solid material that will be suspended by the external structurant. Such post-dosed materials are added later to the structured liquid, under low shear mixing conditions.

Dispersed as an external structurant in the liquid detergent product, pulped citrus fibre has a distinctive appearance. The large aggregates give noticeable on wall drainage and the bulk liquid has a translucent appearance due to high light scattering. Both of these attributes are closer to the properties of HCO and can reinforce the impression of a highly concentrated liquid without need to resort to suspended mica or other visual cues that add non-functional, generally insoluble, appearance-altering chemicals to the detergent liquid. The use of insoluble
materials in concentrated liquids is highly undesirable as it leads to opaque wash liquors and possible unwanted deposition onto the articles being cleaned.

Pulped citrus fibre benefits from air free processing as this improves the stability of the resulting liquids, especially to bottom clear layer separation. This has been demonstrated successfully for 35ml (so called 3x) and 20ml (so called 5x) dose liquids for European sized washing machines (typically 7 to 10 litres fill). Microfibrous cellulose (MFC) has proved extremely difficult to process in a way that prevents bottom clear layer separation for the 20 ml dose liquids.

In order to obtain a satisfactory external structurant is it necessary to process the citrus fibre into a premix and it is also important to apply shear to it more than would be needed just to get it dispersed. The additional energy is advantageous for disruption of the fibres and it may assist with the hydration. The structurant is typically dispersed at very high shear to break up the insoluble fibres and to increase phase volume of the structuring system by maximising break up and contact with anhydrous structuring material. The premix may be left to hydrate further (age) after the high shear mixing.

The concentration of pulped citrus fibre in the pre-mix depends on the ability of the equipment to deal with the higher viscosity due to higher concentrations. The minimum will preferably be at least 1 wt% for practical reasons.

The process gives a stable detergent product with sufficient critical stress, 0.3 Pa, to suspend solid material and suspend itself to give minimal top clear layer separation.

**Surfactant**

In principle, the pulped citrus fibre structurant will structure any type of surfactant containing detergent liquid. However, for cleaning purposes preferred surfactants assist in removing soil from the textile materials or from hard surfaces and assist
in maintaining removed soil in solution or suspension in water. Thus, anionic and/or nonionic surfactants are preferred, more preferably provided in a calcium tolerant blend.

5 Linear alkyl benzene sulphonate (LAS) used on its own is generally calcium intolerant. When required, in order to ensure calcium tolerance, surfactant systems should generally avoid having levels of LAS above 90 wt%. Nonionic-free systems with 95 wt% LAS can be made if some zwitterionic surfactant, such as sulphobetaine, is present. Generally it is preferred to use less than 90 wt% LAS and at least 10 wt% of nonionic surfactant. However, an advantage of the use of pulped citrus fibre over HCO is that it is not necessary to have high levels of nonionic surfactant in the composition. HCO is often added to the mix from a solution in nonionic surfactant and this is therefore limiting for the composition. It is desirable to include only low levels of nonionic, or even to eliminate this component, from detergent compositions designed for high foaming applications. Thus such compositions structured with pulped citrus fibre, advantageously comprise at most 2 wt%, preferably at most 1 wt%, and most preferably zero, nonionic surfactant.

20 Preferred alkyl ether sulphates are C8-C15 alkyl and have 1-10 moles of ethoxylation. Preferred alkyl sulphates are alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C8-C15. The counter ion for anionic surfactants is generally an alkali metal, typically sodium, although other counter-ions such as MEA, TEA or ammonium can be used.

25 Suitable anionic surfactant materials are available as the 'Genapol™' range from Clariant.

Nonionic surfactants include primary and secondary alcohol ethoxylates, especially C8-C20 aliphatic alcohol ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C10-C15
primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkyl polyglycosides, glycerol monoethers and polyhydroxy amides (glucamide). Mixtures of nonionic surfactant may be used. When included therein the composition contains from 0.2 wt% to 40 wt%, preferably 1 wt% to 20 wt%, more preferably 5 to 15 wt% of a non-ionic surfactant, such as alcohol ethoxylate, nonylphenol ethoxylate, alkylpolyglycoside, alkylidimethylamineoxide, ethoxylated fatty acid monoethanolamide, fatty acid monoethanolamide, polyhydroxy alkyl fatty acid amide, or N-acyl N-alkyl derivatives of glucosamine ("glucamides").

Preferred nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C8-C20 aliphatic alcohols ethoxylated with an average of from 1 to 35 moles of ethylene oxide per mole of alcohol, and more especially the C10-C15 primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol.

The Calcium Tolerance Test used herein is that defined in EP1771543. A surfactant blend is prepared at a concentration of 0.7 g/l in water containing sufficient calcium ions to give a French Hardness of 40 degrees. Other electrolytes such as sodium chloride, sodium sulphate, sodium hydroxide are added as necessary to adjust the ionic strength to 0.5M and the pH to 10. The absorption of light of wavelength 540 nm through 4 mm of sample is measured 15 minutes after sample preparation. Ten measurements are made and an average value is calculated. Samples that give an absorption value of less than 0.08 are deemed calcium tolerant.
Water
The compositions are aqueous, that is to say that water forms the majority of the solvent system. Hydrotropes such as propylene glycol and glycerol/glycerine may be used but they will be present at a lesser amount than the water. The minimum water level for an aqueous liquid is 10 wt%. In order to incorporate 0.15% pulped citrus fibre with 20 times its own weight water absorbing capacity it is normal to have a minimum of 3 wt% water added with the pulped citrus fibre (from the premix). For the preferred level of about 0.25 wt% pulped citrus fibre, the amount of water added from a 2.5 wt% premix is 9.75%. Additional water is needed in the composition in order to keep the surfactant, any polymers, soluble builders, enzymes etc in solution. The water amount stated includes both free and any bound water.

Optional Suspended solid material
The suspended material can be any type. This includes perfume encapsulates, care encapsulates and/or visual cues or suspended solid opacifier such as mica or other suspended pearlescent materials and mixtures of these materials. The closer the match of the density of the material to that of the liquid and the thicker the liquid before addition of the external structurant, the higher the amount of material that may be suspended. Typically, up to 5 wt% of insoluble solid material may be suspended stably using the pulped citrus fibre external structuring system, however amounts up to 20 wt% are possible.

Thickeners
Polymeric thickening systems may be added to the liquid to increase the viscosity and further modify the rheology. Pulped citrus fibre is especially compatible with such thickening systems and it is compatible with other external structurants.
Enzymes
In addition to the essential enzyme, one or more further enzymes may be present in a composition of the invention and when practicing a method of the invention. Essential enzymes are lipase and/or cellulase, most preferably lipase. Further enzymes may be selected from the enzymes known to be compatible with surfactant containing compositions, in particular proteases, mannanases and amylases.

**Lipase**:
Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/1 3580, a *Pseudomonas* lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 2 18 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens*, *Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422). Preferred ones have a high degree of homology with the wild-type lipase derived from *Humicola lanuginosa*.


Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ and Lipoclean™ (Novozymes A/S). Also Lipomax™ a lyophilized lipase-preparation from *pseudomonas alcaligenes* (originally from Gist-brocades, more recently from the Genencor division of Danisco).
In addition to, or as an alternative to, lipase one or more other enzymes may be present. However, lipase is particularly preferred. Lipase is preferably included in an amount of from 0.001 to 0.3 wt% active enzyme.

Advantageously, the presence of relatively high levels of calcium in poorly built or unbuilt wash liquors has a beneficial effect on the turnover of certain enzymes, particularly lipase enzymes and preferably lipases from *Humicola*.

The preferred lipases include first wash lipases which comprise a polypeptide having an amino acid sequence which has at least 90% sequence identity with the wild-type lipase derived from *Humicola lanuginosa* strain DSM 4109 and compared to said wild-type lipase, comprises a substitution of an electrically neutral or negatively charged amino acid within 15 A of E1 or Q249 with a positively charged amino acid; and may further comprise:

- (I) a peptide addition at the C-terminal;
- (II) a peptide addition at the N-terminal;
- (III) meets the following limitations:
  - i. comprises a negatively charged amino acid in position E210 of said wild-type lipase;
  - ii. comprises a negatively charged amino acid in the region corresponding to positions 90-101 of said wild-type lipase; and
  - iii. comprises a neutral or negatively charged amino acid at a position corresponding to N94 of said wild-type lipase; and/or
  - iv. has a negative charge or neutral charge in the region corresponding to positions 90-101 of said wild-type lipase; and
- (IV) mixture thereof.
These are available under the Lipex™ brand from Novozymes. A similar enzyme from Novozymes, but believed to fall outside of the above definition is made available by Novozymes under the name Lipoclean™ and this is also preferred.

5 **Cellulase:**
Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera Bacillus, Pseudomonas, Humicola, Fusarium, Thielavia, Acremonium, e.g. the fungal cellulases produced from *Humicola insolens*, *Thielavia terrestris*, *Myceliophthora thermophila*, and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™, Carezyme™, Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation).

8 **Phospholipase:**
Phospholipase may be classified as EC 3.1.1.4 and/or EC 3.1.1.32. As used herein, the term phospholipase is an enzyme that has activity towards phospholipids. Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two fatty acids in an outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric acid in the third position; the phosphoric acid, in turn, may be esterified to an amino-alcohol. Phospholipases are enzymes that participate in the hydrolysis of phospholipids. Several types of phospholipase activity can be distinguished, including phospholipases A₁ and A₂ which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form lysophospholipid; and lysophospholipase (or phospholipase B) which can hydrolyze the remaining fatty acyl group in lysophospholipid. Phospholipase C and phospholipase D (phosphodiesterases) release diacyl glycerol or phosphatidic acid respectively.
Protease:
Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™, Savinase™, Primase™, Duralase™, Dyrazym™, Esperase™, Everlase™, Polarzyme™, and Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OxP™, FN2™, and FN3™ (Genencor International Inc.).

Cutinase:
Cutinase is classified in EC 3.1.1.74. The cutinase may be of any origin. Preferably cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

Amylase:
Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from Bacillus, e.g. a special strain of B. licheniformis, described in more detail in GB 1,296,839, or the Bacillus sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

Peroxidases/oxidases:
Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from Coprinus, e.g. from C. cinereus, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO
98/1 5257. Commercially available peroxidases include Guardzyme™ and Novozym™ 51004 (Novozymes A/S).

**Pectate Lyases:**


Specifically contemplated pectate lyases are disclosed in WO 99/27083 and WO 99/27084. Other specifically contemplated pectate lyases (derived from *Bacillus licheniformis*) are disclosed in US patent no. 6,284,524. Specifically contemplated pectate lyase variants are disclosed in WO 02/006442, especially the variants disclosed in the Examples in WO 02/006442.

Examples of commercially available alkaline pectate lyases include BIOPREP™ and SCOURZYME™ L from Novozymes A/S, Denmark.
Mannanases:

Examples of commercially available mannanases include Mannaway™ available from Novozymes A/S Denmark.

Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic
acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

**Polymers**

Although optional, it is desirable to include soluble polymers in the compositions of the invention. A preferred polymer is modified polyethylene imine PEI 600(20EO). Soil release polymers, especially polyester soil release polymers may also be used. The amount of polymers, when used, is preferably greater than 2 wt%, more preferably greater than 5 wt%, even greater than 10 wt%. Anti-redeposition polymers such as sodium carboxymethyl cellulose may additionally be used.

**Sequestrants**

Although optional, it is desirable to include water-soluble sequestrants in the compositions of the invention. Phosphonate sequestrants are preferred. When included they are advantageously used at levels of from 0.3 to 3 wt%.

**Builders**

Water-soluble builders may be included in the compositions of the invention. The presence of residual citric acid in the citrus fibre, provides a high compatibility with citric acid or citrate based builders.

**Hvdrotropes/neutralising agents**

As mentioned above the compositions are aqueous but the need to keep high levels of surfactants and other water-soluble ingredients in solution may necessitate the presence of additional solvents or hydrotropes. Preferred hydrotropes are propylene glycol, glycerol, glycerine and mixtures thereof. Hydrotropes, when used, are preferably present at levels of from 1 to 20 wt%.

**pH adjustment**
The composition may further comprise MEA and/or TEA and/or sodium hydroxide for alkalinity. As mentioned above it may comprise citric acid. Levels of citric acid preferably range from 0.5 to 5 wt%.

5 **Optical brighteners**

Soluble fabric whitening agents may be included. The use of the external structurant also makes it possible to use insoluble OBA but this is not preferred if it is desired that the liquid is clear (i.e. that it is possible to see through it).

10 **Preservative**

Proxel is a preferred preservative for the liquid compositions. Potassium Sorbate is also preferred.

**EXAMPLES**

15 The invention will now be further described in the following non-limiting examples and with reference to the drawings. Briefly the drawings are:

- Figure 1 is a graph showing rheology for pulped CF at various inclusion levels;
- Figure 2 is a graph showing rheology for pulped CF and HCO with Lipex (24 hours);
- Figure 3 is a graph showing rheology for pulped CF with cellulases;
- Figure 4 is a graph showing rheology for MFC with cellulase; and
- Figure 5 is a graph showing rheology for pulped CF structured liquids with polymers or sequestrant.

NB. In the figures CPF is used to mean pulped citrus fibre (PCF).

In all the following examples, the following abbreviations are used:

- **CF** is Herbacel AQ plus citrus fibre, a powdered citrus peel fruit material ex Herba foods.
- **MFC** is Microfibrous cellulose ex CP Kelco.
HCO is Thixin R hydrogenated castor oil ex Elementis.
LAS is sodium linear alkyl benzene sulphonate anionic surfactant.
LAS acid is acid form of LAS.
SLES is Sodium Lauryl Ether Sulphate with average of 3EO.
SLES(1 EO) is Sodium Lauryl (C12-14) Ether Sulphate with average 1 EO.
LES Nat is Sodium Lauryl Ether Sulphate (SLES 2EO, natural alcohol).
PAS is Sodium Primary Alcohol (alkyl) sulphate (C12-14).
N1 is ethoxylated alcohol nonionic surfactant.
N1 7EO is alcohol ethoxylate 7EO (Neodol 25-7 ex Shell Chemicals).
91-8 is C9-C11 Neodol alcohol nonionic with average 8 moles ethoxylation ex Shell Chemicals.
Empigen® BB is an alkyl betaine ex Huntsman.
CAPB is cocamidopropyl betaine.
Prifac® 5908 is saturated lauric fatty acid ex Croda.
Prifac® 7907 is distilled topped coconut fatty acid ex Croda.
MPG is mono propylene glycol.
PPG is propylene glycol (hydrotrope).
TEA is Triethanolamine.
MEA is Monoethanolamine.
NaOH is 47% sodium hydroxide.
Dequest® 2066 is Diethyleneetriamine penta(methylene phosphonic acid) (or Heptasodium DTPMP).
Dequest® 2010 is HEDP (1-Hydroxyethyldene -1,1,-diphosphonic acid).
Lipex® is Lipex 100L ex Novozymes
Carezyme® is a cellulase ex Novozymes
Endolase® is an endocellulase promoted for its whitening benefits ex Novozymes
Stainzyme 12L is an amylase formulated for liquids ex Novozymes
Mannaway is a mannanase ex Novozymes
EPEI is ethoxylated polyethylene imine cleaning polymer PEI 600 20EO ex BASF.
SRP is Texcare SRN170 polyester soil release polymer ex Clariant.
Acusol® 190 is water soluble polycarboxylate polymeric calcium dispersant ex Dow.
Dowanol DPnB is dipropylene glycol n-butyl ether ex Dow.

Comparative Example A
The powdered Citrus fibre powder was added directly to the prepared detergent liquid and an attempt was made to disperse it using a Silverson high shear mixer. No structuring was formed. The particles of powdered material added did not swell and simply sank to the bottom of the liquid when shear was removed.

Example 1
Premixes of 1 to 2.5 wt% pulped citrus fibre in water were prepared using high intensity mixing. We used a Silverson mixer located in a recycle loop around a batch vessel. The premixes formed were all homogeneous.

Example 2
As an alternative to example 1 we used a high pressure homogeniser was used to supply the shear. Like example 1, a homogeneous well dispersed structured premix was obtained. The maximum premix concentration is limited by the maximum viscosity that the equipment is capable of handling.

Example 3
The pulped citrus fibre premix made in Example 1 or Example 2 (1 or 2 wt% used) was added to a detergent liquid comprising 40 wt% Active detergent (LAS, SLES, Ni 1:1:2) and 15 wt% propylene glycol hydrotrope, the balance being water. Two orders of addition were successfully used:
(3a) Free water, pulped citrus fibre premix then a premixed surfactant concentrate (-60% AD), or
(3b) Free water, surfactant concentrate then pulped citrus fibre premix.

For both processes, it was necessary to use a high intensity mixing step (we used a Silverson L4R mixer) for the combination of the three liquids. Successful structuring has been demonstrated down to 0.15% pulped citrus fibre in the final detergent liquid. We have found that avoidance of aeration during processing is advantageous. If too much air is incorporated (especially at very low levels of the structurant), the structure has been shown to be destabilised by small air bubbles leading to bottom clear layer separation.

Example 4

Part A: Structurant pre-mix
A structurant pre-mix was prepared using 2% Herbacel plus AQ (type N) citrus fibre powder, 97.9% tap water and 0.1 % Potassium Sorbate preservative. The pre-mix was prepared using a pilot plant scale Gaulin high pressure Homogeniser operating at 350 bar. The resulting pulped citrus fibre (PCF) pre-mix was readily handleable and pumpable.

Part B: Concentrated base detergent liquid
In a separate vessel from the structurant premix A, a concentrated base detergent liquid B, having the composition shown in Table 1 (except for the 2 wt% PCF pre-mix and the perfume) was prepared using a 50 litre capacity pilot plant vessel equipped with a mixing element of the 'Flexible Agitator System (FAS)' geometry. 12.5% of the water had been removed from the formulation to allow for post dosing of the 2% PCF pre-mix: Part A. The concentrated mixture was allowed to de-aerate for > 1 hr.
Table 1: Composition of Structured liquid of Example 4

<table>
<thead>
<tr>
<th>Material</th>
<th>Activity</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100</td>
<td>9.67</td>
</tr>
<tr>
<td>Glycerol</td>
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<td>5.12</td>
</tr>
<tr>
<td>PPG</td>
<td>100</td>
<td>9.21</td>
</tr>
<tr>
<td>NaOH</td>
<td>47</td>
<td>5.87</td>
</tr>
<tr>
<td>TEA</td>
<td>100</td>
<td>3.32</td>
</tr>
<tr>
<td>NI 7EO</td>
<td>100</td>
<td>20.59</td>
</tr>
<tr>
<td>Citric acid</td>
<td>50</td>
<td>2.01</td>
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<tr>
<td>LAS acid</td>
<td>97.1</td>
<td>13.71</td>
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<tr>
<td>Prifac 5908</td>
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<td>4.89</td>
</tr>
<tr>
<td>SLES</td>
<td>70</td>
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<tr>
<td>PCF</td>
<td>2</td>
<td>12.80</td>
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<tr>
<td>Perfume</td>
<td>100</td>
<td>1.42</td>
</tr>
<tr>
<td>TOTAL</td>
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<td>100.00</td>
</tr>
</tbody>
</table>

Combining structurant pre-mix A with Concentrated base detergent liquid B

The concentrated base detergent mixture B was circulated via a 150/250 Silverson high shear mill by means of a recycle loop to ensure all lines were fully primed and purged of air. Flow rate 1450 l/hr (single pass residence time in mill 0.1 seconds). The Silverson mill was turned on at 6250 rpm (9063 w/kg) to simulate large scale operating conditions. Then the structurant Pre-mix A was dosed into the main recirculation loop close to the high shear mixer inlet to minimise interaction between the streams prior to intimate dispersion. The perfume was then added using low shear mixing.

The pulped citrus fibre structured liquid was then sampled and its rheology measured. Again, after 1 week storage at ambient temperature, the rheology was
remeasured and the samples were visually assessed to see if there was either top clear layer separation or bottom clear layer separation.

The required rheology for thickening and suspending duty was obtained and maintained and no separation was observed.

**Example 5 - Varying the amount of structurant**

Example 4 was repeated, but the amount of PCF in the premix A was varied so that when it was added to concentrated base detergent mix B the final level of PCF in the detergent liquid was only 0.12%. The rheology of this liquid was not sufficient for suspending duty. See Figure 1, which shows that at 0.12% PCF there was insufficient formulation stability and viscosity build (low critical stress).

It is thought that this was due to insufficient PCF being present to establish a stable network with which to provide suspending duty. Then the process was repeated to form a liquid with 0.16 wt% PCF external structurant. After storage for a week, this liquid was showing signs of top clear layer separation. This was at the margins of acceptability. It is possible that a different process, or a different composition for the detergent liquid in Part B, could have generated structure even at this low level, but it must be regarded as a less preferred level for structurant inclusion and indicates a lower end of the range of 0.15%. Finally, the level of PCF structurant was increased to 0.32%. We have found that the combination of the level and the obtaining of a yield stress (via the processing conditions and the other ingredients present) is significant for effective structuring.

Lipase could be added to Example 4 and Example 5 liquids structured with PCF without loss of structuring.

**Example 6 and Comparative example B - Lipase resistance of structurant**

The base composition of the Liquid used for examples 6 and comparative example B is given in Table 2:
Table 2 - Compositions of Example 6 and Comparative Example B Liquid

<table>
<thead>
<tr>
<th>Material</th>
<th>Activity</th>
<th>Weight %</th>
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<tbody>
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<td>Glycerine</td>
<td>100</td>
<td>5.00</td>
</tr>
<tr>
<td>MPG</td>
<td>100</td>
<td>18.00</td>
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<td>NI 7EO</td>
<td>100</td>
<td>12.7</td>
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<tr>
<td>LAS acid</td>
<td>97.1</td>
<td>8.5</td>
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<td>Prifac 5908</td>
<td>100</td>
<td>3.0</td>
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<tr>
<td>SLES</td>
<td>70</td>
<td>4.2</td>
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<td>100</td>
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<td>PCF*</td>
<td>2</td>
<td>0.25</td>
</tr>
<tr>
<td>NaOH</td>
<td>47</td>
<td>To pH 7</td>
</tr>
<tr>
<td>Water</td>
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<td>To 97%</td>
</tr>
<tr>
<td>TOTAL</td>
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<td>97.00</td>
</tr>
</tbody>
</table>

Comparative example B, representing the prior art, was structured with 0.25 wt% HCO, crystallised from a hot melt, in place of the PCF in table 2.

The 3% "hole" was filled with either Lipex® 100L or a 30 parts sorbitol/64parts demin. water, i.e. the solvent/stabiliser for commercial samples of Lipex.

Rheology was measured at 25°C using an Anton Paar ASC rheometer.

Figure 2 shows the rheology data after 24 hours. Comparative example B shows that when using Lipex in an HCO structured liquid there is complete loss of structuring within 24 hours at ambient temperature. In contrast, Lipex has no effect on the otherwise identical liquid structured with PCF, as in example 6.
Example 7 and Comparative example C - Cellulase resistance of structurant.
Cellulase was not tested on HCO, as it was not expected that cellulase would have any effect on such an oily material. For example 7 two types of cellulase were added to a liquid detergent structured with 0.25% PCF, as described in Example 4.

Figure 3 shows the effect of adding each type of cellulase at 1%. It can be seen that for both Carezyme and Endolase there is no significant effect on the rheology after 2 weeks storage at 37°C. Figure 4 shows the corresponding result for Comparative example C, which is a detergent liquid structured by dispersing a premix of 0.1 wt% MFC using a process analogous to Example 4 above. It can be seen that for the addition of cellulase (Carezyme 1%) @ 37°C; there is an initial drop in plateau viscosity which may be caused by the cellulase attacking part of the structurant, but not causing it to fail as catastrophically as the HCO formulated with lipase. It is clear that this causes a reduction in the range between the resting viscosity (no shear) and the pouring viscosity (high shear); this range is already lower than that obtained with the PCF structured example 6.

Examples 8 to 26 further examples of detergent liquids structured with PCF.
Table 3 shows a range of heavy duty laundry detergent liquids that may be structured with pulped citrus fibre. Examples 8, 9, 10 and 11 are so called 3 times concentrated laundry liquid suitable for use at approx 35 ml dose to a standard European front loading automatic washing machine. Examples 12, 13, and 14 are compositions suitable for use at a 20 ml dose to the same type of machine.
Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>Example 8</th>
<th>Example 9</th>
<th>Example 10</th>
<th>Example 11</th>
<th>Example 12</th>
<th>Example 13</th>
<th>Example 14</th>
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<tr>
<td></td>
<td>% as 100%</td>
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<td>% as 100%</td>
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<td>Lipex or Lipoclean 100L</td>
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<td>0.01</td>
<td>0.01</td>
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<td>1.39</td>
<td>1.39</td>
<td>2.43</td>
<td>2.43</td>
<td>2.43</td>
<td>2.43</td>
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<tr>
<td>Water and impurities</td>
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<td>57.67</td>
<td>27.94</td>
<td>37.4</td>
<td>29.77</td>
<td>27.15</td>
<td>20.435</td>
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<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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</tbody>
</table>

Table 4 shows the rheology obtained by variants of Examples 12 and 14. The composition examples 15 to 18 were tested as described above to obtain the rheology profiles shown in Figure 5; without yet adding in the enzyme. Based on the findings for the lack of effect of Lipase on similar compositions the addition of
the Lipase would not affect the Rheology. Lipase and cellulase can be added without affecting the stability of the rheological profile over time. These examples show that the rheology is usefully obtained with the inclusion of various levels of cleaning and soil release polymers, also the addition of high levels of polymer and the addition of relatively high levels of sequestrant. All of these ingredients might have had a detrimental effect on the rheology.

Table 4

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<thead>
<tr>
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<th>Example 15</th>
<th>Example 16</th>
<th>Example 17</th>
<th>Example 18</th>
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<td>Glycerine</td>
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<td>1.5</td>
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<td>Dequest 2010</td>
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<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
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<tr>
<td>Water</td>
<td>balance</td>
<td>Balance</td>
<td>balance</td>
<td>balance</td>
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</tbody>
</table>

*A 3% hole was left in the base to accommodate the lipase enzyme.*
Table 5 - Household cleaners

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<th>Ingredients (%) wt</th>
<th>Example 19 (Kitchen cleaner)</th>
<th>Example 20 (Bathroom cleaner)</th>
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<tr>
<td>Water</td>
<td>89.86</td>
<td>90.29</td>
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<tr>
<td>91-8</td>
<td>5</td>
<td>3.5</td>
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<tr>
<td>Acusol 190 (24.8% active)</td>
<td>0.5</td>
<td>0.5</td>
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<td>Citric acid pH4</td>
<td>1</td>
<td>4</td>
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<tr>
<td>MEA</td>
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<td>-</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.3</td>
<td>0.29</td>
</tr>
<tr>
<td>Dowanol DPnB</td>
<td>1</td>
<td>-</td>
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<td>Preservative</td>
<td>0.016</td>
<td>0.016</td>
</tr>
<tr>
<td>Prifac 7907</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Silicone DB31 0 (36.2% active)</td>
<td>0.001</td>
<td>-</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>0.893</td>
<td>1.154</td>
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<tr>
<td>PCF</td>
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<td>0.25</td>
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</tbody>
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Table 6 - Dish Washing Liquids

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<tr>
<th>Example (%wt)</th>
<th>21</th>
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<th>23</th>
<th>24</th>
<th>25</th>
<th>26</th>
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<tr>
<td>LAS</td>
<td>10.50</td>
<td>11.81</td>
<td>19.65</td>
<td>11.55</td>
<td>0.00</td>
<td>2.54</td>
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<td>SLES 1EO</td>
<td>3.06</td>
<td>3.45</td>
<td>0.00</td>
<td>2.19</td>
<td>8.75</td>
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<td>LES Nat</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
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<tr>
<td>PAS</td>
<td>0.44</td>
<td>0.49</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>CAPB</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.70</td>
<td>2.89</td>
<td>0.96</td>
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<tr>
<td>MgSO4. 7H2O</td>
<td>0.61</td>
<td>0.66</td>
<td>0.00</td>
<td>0.00</td>
<td>0.20</td>
<td>0.00</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.96</td>
</tr>
<tr>
<td>Urea</td>
<td>0.00</td>
<td>0.00</td>
<td>4.38</td>
<td>2.63</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>Ethanol</td>
<td>10.50</td>
<td>11.81</td>
<td>19.65</td>
<td>11.55</td>
<td>0.00</td>
<td>2.54</td>
</tr>
<tr>
<td>PCF</td>
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<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
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<tr>
<td>Preservative</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
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<tr>
<td>Water</td>
<td>To 100</td>
<td>To 100</td>
<td>To 100</td>
<td>To 100</td>
<td>To 100</td>
<td>To 100</td>
</tr>
</tbody>
</table>

Where not already present all of the liquids in examples 19 to 26 can simply be reformulated to contain Lipase and/or cellulase at levels of from 0.0001 to 5 wt%, preferably from 0.001 to 0.3 wt%. The structuring rheology is not affected by such enzyme inclusion.
Claims

1. A structured aqueous liquid detergent composition comprising:
   at least 10 wt% water,
   at least 0.5 wt% surfactant,
   at least 0.0001 wt% of enzyme selected from lipase, cellulase and mixtures thereof.
   an external structurant,
   characterised in that the external structurant comprises at least 0.15 wt%,
   preferably at least 0.2%, citrus fibre that has been mechanically pulped and swollen in water.

2. A composition according to claim 1 comprising 0.16 to 0.35 wt% pulped citrus fibre.

3. A composition according to any preceding claim with a yield stress greater than 0.2 Pa.

4. A composition according to any preceding claim in which the pulped citrus fibre is derived from lemons or limes.

5. A composition according to any preceding claim in which the enzyme comprises lipase, preferably 0.001 to 0.3 wt% active enzyme.

6. A composition according to any preceding claim further comprising suspended insoluble material.

7. A composition according to any preceding claim comprising at least 1.5 wt%, preferably at least 2.5 wt% water-soluble polymers.
8. A composition according to claim 7 in which the polymers are selected from the group consisting of modified ethoxylated polyethylene imines, polyester soil release polymers and mixtures thereof.

9. A composition according to any preceding claim comprising at least 2.5 wt% anionic surfactant.

10. A composition according to claim 9 comprising at least 10 wt% anionic surfactant.

11. A composition according to any preceding claim comprising at least 3 wt% nonionic surfactant.

12. A high foaming composition according to any one of claims 1 to 10 comprising at most 2 wt% nonionic surfactant.

13. A composition according to any preceding claim comprising at least 25 wt% total detergent surfactant.

14. A process to manufacture a pulped citrus fibre structured detergent liquid comprising at least 0.15 wt% pulped citrus fibre structurant and at least 0.5 wt% surfactant, the process comprising the steps of:
   a) Selecting a citrus fruit material, preferably one with low sugar content, comprising citric acid or citrate,
   b) forming citrus fibres from the citrus fruit material, preferably by extraction,
   c) subjecting the citrus fibres to mechanical processing comprising application of shear in the presence of at least 15 times the amount of water based on the citrus fibres, the shear being sufficient to cause
structural disruption and hydration of the citrus fibres to form a structuring premix comprising dispersed pulped citrus fibre; and
d) further dispersing the pulped citrus fibre structuring premix into a de-aerated detergent liquid to form an externally structured detergent liquid comprising surfactant; and
e) adding enzymes selected from lipase, cellulase and mixtures thereof to the externally structured detergent liquid.

15. A process according to claim 14 in which the detergent liquid in step (d) contains citrate builder.
Figure 5

[Graph showing viscosity vs. shear stress for different samples: EG 15 Base plus eq water, EG 16 Base plus EPBI, betaine, SRN170, EG 17 Base plus EPBI, betaine, SRN170 and Dequest, EG 18 Base plus Dequest.]
INTERNATIONAL SEARCH REPORT

PCT/EP2011/067549

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) and both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. X See patent family annex.

* Special categories of cited documents :
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"A" document member of the same patent family

Date of the actual completion of the international search: 3 February 2012
Date of mailing of the international search report: 17/02/2012

Name and mailing address of the ISA:
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, 340-2041
Fax: (+31-70) 340-3016

Authorized officer: Loi sel et-Tai sne, S
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