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(54) **Detergent compositions.**

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Description

This invention relates to fluid compositions, particularly detergent compositions, comprising a continuous and one or more discontinuous phases, the fluid stably containing small bubbles of gas.

One aspect of the invention relates to compositions in which gas bubbles of a particular size range remain dispersed. Applicants have not only discovered the gas bubble component of compositions, but have also discovered how control and refinement of incorporation of these bubbles into compositions imparts a surprising stability against phase separation. A further aspect of the invention is a process for stabilising compositions by the incorporation of gas bubbles. Most particularly, the invention relates to compositions which comprise solid particles of a very small size (less than 5 microns) and a process for stabilising compositions by incorporation of gas bubbles therein.

It has now been found that compositions with a continuous and one or more discontinuous phases can be rendered quite stable against separation into different phases, a phenomenon known as syneresis, by incorporating bubbles of gas having diameters of from 3 to 150 microns, with the average diameter being from 3 to 45 microns. The resulting "aerated" composition is greatly more stable against separation over longer storage times and high temperatures then the non-aerated composition. This stability is an important characteristic: stable compositions not only provide a generally identical mix of components from one dose to the next, they also avoid the appearance of unattractive separation layers.

Compositions of the present invention comprise a continuous and one or more discontinuous phases together with from about 1% up to about 20% by volume of gas in bubbles having diameters of 3 to 150 microns. A surfactant must also be present. The bubbles are present throughout the continuous phase of the composition, which also has one or more non-gaseous discontinuous phases dispersed throughout. The continuous phase of the invention is generally liquid, although ingredients in the continuous or one of the discontinuous phases may impart a high viscosity or thixotropy to the composition, making the total composition a gel, paste or soft solid. The compositions coming within the invention cover a wide range of materials. They may comprise a liquid continuous phase with a liquid or solid discontinuous phase and may be aqueous or non-aqueous. They are generally useful as detergent cleaning compositions, such as mechanical dishwashing, hard surface or fabric washing compositions. These particular types of compositions only illustrate and do not limit the scope of the compositions within the invention.

(The term "aeration" used in describing the invention herein is understood to refer to an incorporation of any gas into a composition, not only air. "Aerated" compositions should be understood to include air or any other suitable gas such as those identified below.)

BACKGROUND OF THE INVENTION

Phase incorporation of gas or gas bubbles is known for many uses. Flotation technology for instance relies on introduction of gas bubbles, generally discussed at Kirk-Othmer Encyclopaedia of Chemical Technology, 2nd Edition, (J Wiley & Sons 1966), Vol 9, pp 380-398. Flotation separates one mineral species from another based on the different wettability of the mineral surfaces. Gas is bubbled into water containing a frothing agent and impure, ground minerals. The mineral particles with affinity for the air bubbles rather than water rise through the water into a surface froth to be separated from the minerals that are more wettable.

The frothing agent added to water selectively controls the wettability of the minerals. An air bubble usually does not adhere to a clean mineral surface. However, in the presence of a suitable frothing agent, the mineral acquires a hydrophobic coating and an air bubble may attach quite readily. The greater the affinity between the hydrophobic mineral surface and the bubble, the larger the area of surface area contact between the bubble and mineral will be, and the smaller the contact angle between the two is.

GB 2 140 451 (Lion Corp) describes a liquid detergent composition which contains a polishing agent and has non-skin roughness. The composition has alkyl polyethoxylene sulphate and amine oxide as surfactants; clay as thickening and stabiliser; an insoluble scouring powder of average particle size 1 to 150 microns; and 2.5% to 8.5% by volume of gas bubbles having 0.1 to 0.7 millimetre average diameter. Substantially all the bubbles are smaller than 1.5 millimetres in size. If the amount of amine oxide exceeds 5% by weight, the dispersion stability is lost. GB 1 304 080 (Colgate) permits bubbles of 0.1-4 millimetres in size in dentifrice compositions.

Bubbles have also been incorporated into liquid detergent compositions. Thus, GB 2 140 451 (Lion) and JP 60/076598 (Lion) incorporate gas bubbles of 0.1-0.7 millimetre and 50-700 microns diameter respectively into their liquid detergents.

SUMMARY OF THE INVENTION

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

(a) from about 5 to 40% by weight of a particulate detergent builder;
(b) a liquid continuous phase;
(c) a surface active agent; and
(d) from about 1 to 20% by volume of a gas present as bubbles ranging in diameter from 3-150 microns and having an average diameter from 3-45 microns;

the overall density of the composition being from 85% to 115% of the density of the liquid continuous phase alone.

DETAILED DESCRIPTION OF THE INVENTION

It is seen that aerated compositions are not new. What is new is the refinement by applicants of such compositions and the process of making them. The compositions of the invention incorporate bubbles, but within the following limits: 1% to 20% by volume of gas is present as bubbles which range in size from 3 to 150 microns, and have an average size of 3 to 45 microns.

When gas is present within these limits in compositions having a continuous and one or more discontinuous phases, and incorporating a surface active agent, it is found that the gas imparts a surprising stability against phase separation to the compositions. The stability of these aerated compositions is believed to be due not to any structured liquid effect, eg lamellar phase structures, but rather to the interaction of the gas bubbles with the one or more discontinuous phases. Though dispersed throughout the continuous phase, the bubbles appear to co-operate with only the one or more discontinuous phase materials. The bubbles appear to reduce the density of the one or more discontinuous phase materials to a value close to the density of the continuous phase. The stability of the compositions is believed to result from this substantial equalisation of the density of the continuous with the one or more discontinuous phases.

From this explanation, it should be clear that the one or more discontinuous phases of compositions of the invention have a density which is greater than that of the continuous phase. If there are multiple discontinuous phases in a composition, that composition may still benefit from aeration if the average density of all the discontinuous phases is substantially greater than the density of the continuous phase.

It has been found that when the volume of gas incorporated in the mixture of the continuous and one or more discontinuous phases renders the density of the one or more discontinuous phases (D^*_{discon}) equal to, or within from 85% to 115% of the density of the continuous phase, the composition has increased stability.

Thus, applicants do not suggest that any amount of aeration within a certain range will stabilise a composition. Aeration to a D^*_{discon} level that is greater than 115% of the continuous phase density will not stabilise the composition: phase separation with a clear liquid layer at the top may result. If aeration to a D^*_{discon} level of less than 85% of the continuous phase density is performed, then phase separation with a clear liquid layer on the bottom may result. The latter is a type of reverse phase separation with the lower density discontinuous phase appearing above a separated continuous phase.

The compositions of the invention resist separation, not only over long storage periods at ambient temperature, but also over long times at elevated temperatures (37 °C). Surprisingly, the gas bubbles remain in the composition during exposure to these elevated temperatures and do not dissolve, coalesce into larger bubbles or rise to the surface of the composition to any significant degree.

The size of gas bubbles incorporated into compositions of the invention has been found important. The bubbles are effective to stabilise the compositions when they range in size from 3 to 150 microns. Bubbles of less than about 3 microns are found to have a tendency to dissolve in the continuous phase, while those larger than about 150 microns usually rise to the uppermost surface of the composition and/or coalesce with other bubbles. It is found that if a majority of the bubbles either dissolve in, or rise to the surface of the continuous medium, they no longer impart a stabilising effect. The optimal average bubble diameter is 3 to 45 microns: bubbles of this size tend not to dissolve or rise out of the composition.

Because compositions of the invention may be made under large-scale industrial conditions, fine control of bubble sizes will not always be practicable. It is expected the aeration processes to be used (discussed below) will generate a range of non-uniform bubble sizes only partly within the range of 3 to 45 microns. Bubbles outside this range are not expected to decrease stability in the compositions if at least 70% of the bubbles are within the 3 to 45 microns range, preferably if 85% of the bubbles are within that range and, most preferably, if 90% or more fall within 3 to 45 microns.

Depending on the process of aeration, described below, one may obtain either a wide or narrow range of bubble sizes. A wide distribution of non-uniform bubble sizes over the 3 to 45 micron range is acceptable. However, it is also acceptable to have a narrower cut of bubble sizes such as 10 to 40 microns to reduce or avoid bubble dissolution or rising. Alternatively, an even narrower range of 15 to 30 microns is acceptable as this range is believed to cover the size of bubbles least likely to dissolve or coalesce with other bubbles.

It is also preferred that the gas bubbles be evenly dispersed through the compositions of the invention. So as to avoid such variations, with local syneresis as a possible result, the gas bubbles should be distributed evenly through the entire composition.

Suitable gases for incorporation in the composition are those which do not damage or interact with the composition's components. Such gases include the noble gases as well as nitrogen, oxygen, air, and carbon dioxide. In addition to these gases, others such as aerosol propellants, which are halogenated hydrocarbons may be used, providing that they are not too soluble in the phases of the composition.

As stated above, an important aspect of the invention is the realisation that gas bubbles incorporated into a liquid continuous phase appear to lower the density of the solid discontinuous phase suspended therein to a value roughly equal to that of the liquid continuous phase. The amount of gas needed to render the density of the solid roughly equal to that of the liquid may be easily calculated. Density is, of course, equal to mass divided by volume (D = M/V). Since the incorporation of gas in a composition increases its volume more than weight, the density of the solid discontinuous phase modified by gas may be expressed as

$$D^*_{discon} = M_{discon}/(Volume_{discon} + Volume_{gas})$$

The mass of gas modifying the discontinuous phase may be disregarded as too small to matter.

The composition achieves stability when D^*_{discon} is set equal to the density of the liquid continuous phase (D_{cont}). Thus, one may obtain the volume of gas to be added to a composition from the equation

$$M_{discon}/(Volume_{discon} + Volume_{gas}) = M_{cont}/Volume_{cont}.$$

All the values in the expression save $Volume_{gas}$ may be readily measured or determined theoretically, making calculation of the volume of gas to be incorporated a simple matter. (This volume may in turn be converted to a weight percentage, if desired, of the final stabilised composition by multiplying the volume of gas by the density of that particular gas.) When the density of the one or more discontinuous phases is reduced by aeration with $Volume_{gas}$ to a level between 85% D_{cont} to 115% D_{cont}, then the resulting composition has surprisingly improved stability against phase separation.

Compositions of the invention may have from 1 to 20% by volume of gas incorporated therein to achieve stability. For compositions described below, it has been observed that from 3 to 15%, or 8% to 10% gas by volume may stabilise the composition.

Since the gas may be added in such an excessive amount, which does not stabilise the composition, it is important to determine the amount of gas needed to bring the density of continuous and discontinuous phases into proximity. To do so requires knowledge of the density of the different phases.

The density of the continuous and discontinuous phases may be calculated or measured before being mixed together. The calculated or experimental value for the continuous or discontinuous phase density may be used to determine the amount of gas to be incorporated. Depending on the process of incorporating gas into the compositions, one may have to run a series of plant trials to determine the time required to aerate the composition to a sufficient but not an excessive degree.

The continuous phase may be aqueous or non-aqueous. Examples of non-aqueous fluids are described in GB 2 194 546 (Colgate) and include nonionic materials.

It has been found that for the gas bubbles to be retained within the composition so as to impart stability, a surfactant should be present. Only very low levels are required. For example, in a detergent composition only 0.0001 wt % may be necessary. A suitable range for incorporation is from 0.001 wt % to 0.5 wt %, preferably 0.05 to 0.4 wt %.

Many types of surfactants may be used in the cleaning compositions of the invention, including anionic, nonionic, zwitterionic and amphoteric. The anionic surfactants include soaps, alkyl benzene sulphonates, primary alkyl sulphates, secondary alcohol sulphates, linear ethoxy sulphates and alpha-olefin sulphonates. The alkyl chains in these anionics may suitably be from 8 to 22 carbons long. When ethoxylated, the anionics suitably have from 1 to 8 ethylene oxide groups. The nonionic surfactants may suitably be alkoxylated fatty alcohols or fatty amides, the alkyl groups having from 6 to 20 carbons and the alkoxyl groups having from 2 to 4 carbons. There may be from 1 to 10 alkoxyl groups per molecule. Other suitable nonionics include block copolymers such as Pluronics and Tergitols. Zwitterionic surfactants may be present as well. When amine oxides are used as surfactants, they should be present at over 5% by weight.

The discontinuous phase may preferably be an alkali-metal condensed phosphate present in the composition as a water hardness sequestering agent or builder. Tripolyphosphate is the preferred sequestrant although pyrophosphate, hexametaphosphate, or other condensed phosphates may be used. The sequestrant may be present in the formula from about 5% to 40%, with 15% to 25% by weight being more preferred. Use of the sequestrant, such as sodium tripolyphosphate in excess of its solubility limit within the formula, requires that the solid be present as particles suspended in the composition. The presence of solids will affect the viscosity of the liquid. Other inorganic builders which may be used are sodium and potassium salts of polyphosphate, orthophosphate, carbonate, bicarbonate, sesquicarbonate and borate. Other detergent builders can also be used in the present invention. They are generally sodium and potassium salts of the following: citrates, nitrilotriacetates, phytates, polyphosphates, oxydisuccinates, oxydiacetates, carboxymethyloxy succinates, tetracarboxylates, starch and oxydised heteropolymeric polysaccharides. Sodium citrate is an especially preferred builder.

Water-insoluble aluminosilicate ion-exchange materials may be used as alternative builders. These are crystalline or amorphous materials of general formula

$$(Cat_{2/n}O)_x.Al_2O_3(SiO_2)_y.ZH_2O$$

wherein Cat is a cation having a valency n that is exchangeable with calcium (eg Na^+ or A^+); x is a number from 0.7 to 1.5; y is a number from 1.3-4; and Z is such that the bound water content is from 1% to 28% by weight. Preferred is the commercially-available product Zeolite Type A:

$$Na_2O.\ Al_2O_3.\ 2SiO_2.\ 4.5H_2O$$

Suitable adjuncts to the cleaning or detergent compositions include enzymes, bleach and softeners. The pH of the present compositions will generally be in the slightly alkaline range. When enzyme is present the pH is preferably from 5 to 9. When chlorine bleaches are present, it is preferable to keep the pH in the 8 to 13 range in order to preserve chlorine activity.

One cleaning composition that could be further improved by aeration is a thixotropic liquid machine dishwashing composition described in our co-pending European patent application 0 316 152. The dishwashing composition must be a uniform mixture of ingredients to deliver the optimum combination of active components with each dose. Consequently, the aeration of the present invention would be very useful in contributing to the stability of the composition of our copending EP 0 316 152.

The dishwashing composition has high viscosity when at rest but undergoes a viscosity decrease under the influence of applied shear. The preferred compositions have a reversible decrease in viscosity with time after removal of the shear. Agitation of the liquid in its container, such as shaking or squeezing, supplies sufficient shear strain to initiate shear-thinning behaviour and increased liquid flow. The liquid should quickly regain its structure after pouring. These liquid characteristics are termed "thixotropy".

The thixotropic dishwashing composition is aqueous and comprises 25-30 wt % of an alkali-metal builder and 25-30 wt % of an alkali-metal silicate, a stabiliser system comprising 0.05-5% by weight of an alkyl phosphate, phosphonate, sulphate or sulphonate with from 10% to 15% gas present as bubbles ranging in size from 3 to 45 microns. The composition further comprises a detergent active. The continuous phase of the formulation comprises the water and metal silicate, while the non-gaseous discontinuous phase comprises solid particles of the builder material. (Usually under 5% of the builder dissolves in the aqueous phase.) Any detergent actives are believed to associate with the solid builder particles.

It has been discovered that aeration in the presence of surfactant improves the stability of the liquid composition. It is not believed that aerated compositions with alkyl derivatives have previously been described as stable systems.

The liquid dishwashing compositions may also preferably incorporate a bleach, eg. a hypochlorite, which may be present in the continuous phase at 0.5 to 5 wt %. The system is stable when these bleaches are included in comparison to some systems of the prior art, wherein the presence of hypochlorite destroys system stability.

The dishwashing composition has improved rheology and stability and can deliver a high and uniform dosage of active ingredients to the machine wash cycle.

The system has good stability against physical separation upon storage, providing a more uniform product. Poor physical stability can lead to development of a stratified liquid through separation of a fluid layer and a solids layer. This requires remixing by the end user through vigorous shaking of the container.

The structuring system may also be adjusted to develop optimum fluid rheology in terms of low shear rate attributes, giving physical stability, cup retention and moderate shear rate flow behaviour during dispensing into the wash cycle.

The product according to the present invention may be a thixotropic machine dishwashing detergent in the form of a slurry-like paste. The product possesses a viscosity of between 5-50 Pas at $0.9s^{-1}$ and a viscosity between 500-5000mPas at $20s^{-1}$ (Haake RV2 at 20 ° C, MV2 rotor).

The stabilising alkyl derivatives may be long chain alkyl, ie C_{10}-C_{22}, sulphates, sulphonates, phosphates, phosphites, or phosphonates. Preferred are phosphorous based compounds, which also assist in foam dispersion.

Most preferred is the commercial product stearyl phosphate 7062 (Marchon) or the mixture of C_{16}/C_{18} alkyl dihydrogen phosphate and dialkyl hydrogen phosphate, referred to hereafter as ALF-5 (Dow Chemicals).

The higher alkyl phosphates and phosphonic acids are also preferred due to their tendency to reduce corrosion of metals and erosion of vitreous enamel surfaces.

If sulphates or sulphonates are to be used, such as alkyl benzene sulphonates, it is preferred to additionally use a phosphate or phosphonate.

The applicants have further discovered optimal compositions in which very small particles of a solid are dispersed through the continuous phase which may be stabilised by the incorporation of gas bubbles. Substantially all of the solid particles are less than 5 microns in size. Preferably, at least 90% of the particles are smaller than 4 microns and, even more preferably, at least 75% of the particles are smaller than 2 microns. Up to about 5% of the particles may be larger than 5 microns. The smallest particles may be under 1 micron in size; however, no exact minimum particle size is determinable due to the difficulty of measuring particle sizes of 1 micron or less.

The gas bubbles are believed to contribute to stabilisation of the composition, possibly by interaction with the solid particles (which may form a network) in a manner resembling the bubble-particle interaction in the flotation technology. The particles here may be coated with active, as the active is not seen to appear in the liquid active phase. Such a hydrophobic particle would, presumably, be able to form a large area of contact with a gas bubble. The applicants offer this possibility as an aid to understanding the invention which, however, in no way limits the scope of the invention. Thus, the analogy to flotation technology is not deemed to be an exact one because the purpose of flotation technology is to separate materials whereas any bubble-particle interaction here acts to maintain the composition in a stable form. Additionally, of course, the bubbles in flotation technology are very mobile, whereas it is desired that the bubbles in the compositions of the invention do not rise to the surface.

The particles present in the thixotropic, aqueous liquid cleaning composition may be comprised of sodium tripolyphosphate hexahydrate crystals. Although the STP, when added, is usually an anhydrous product having a size range of nearly 1 cm, the crystals of STP hexahydrate in the compositions are very small.

Part of the STP hexahydrate of the compositions may be replaced by other materials, eg other phosphate and/or builder salts including zeolites, or water-insoluble clays. It is preferred, however, that at least 30% of the particles less than 5 microns in size which contribute to stability be STP hexahydrate.

It is noted that the recrystallisation of STP to a network of very small STP 6aq particles is solely responsible for the high viscosity and shear thinning behaviour of the liquid. It is preferred that the composition should have a viscosity of 15-30 PaS at 0.9 s^{-1} and 2-6 PaS at $20s^{-1}$ as measured at RTP on a Haake viscometer.

The sources of alkalinity are used in combination in the more preferred embodiments of this invention. These become part of the aqueous continuous phase. An alkali-metal carbonate may be used as an alkaline buffering agent and may be present from 0 to 30 wt%, or more preferably from 2 to 10 wt%.

Pure alkali-metal metasilicates or alkali-metal silicates with a molar ratio of SiO_2/Na_2O and/or K_2O of from 2.0 to 3.25 may be used as alkaline sources and as anti-corrosion agents to protect metal and china surfaces against the harshly alkaline environments present in the wash. The silicate may be used in the form of an aqueous liquor or a solid and may be present in the formula from 0.1 to 40 wt% or 0.1 to 30 wt%, more preferably from 10 to 25 wt%.

An alkali-metal hydroxide may be used as an alkaline source and as a means to boost the pH of the liquid detergent concentrate to stabilise the hypochlorite. Sodium or potassium hydroxide in the form of an aqueous liquor or as a solid may be used in the formula at from 0.1 to 9 wt%, preferably from 0.5 to 7 wt%.

Polymers may be added to the system to provide a further building effect. These polymers constitute part of the continuous phase. The polymer used should be of a synthetic type and be water-soluble. Examples of applicable polymers are polyacrylic acid and its alkali-metal salts, polymethacrylic acid and its alkali-metal salts, and copolymers of these with alkyl acrylates and alkyl methacrylates, copolymers of these with maleic anhydrides, polyacrylamide and partially hydrolysed polyacrylamide, polyacrylonitrile and its partially hydrolysed forms, polymethacrylonitrile and its partially hydrolysed forms, polystyrenesulphonic acid and its alkali-metal salts, polymaleic anhydride and its alkali-metal salts, poly n-vinyl lactams (polyvinyl pyrrolidone, poly(N-vinyl caprolactam, etc), and polymers of N-substituted acrylamides or mixtures thereof. These polymers have a weight average molecular weight of from 1,000 to 15,000,000 with a molecular weight of from 10,000 to 400,000 preferred, and 100,000 to 250,000 most preferred. These polymers may be used in the acid or the neutralised form. The polymers should be of a hypochlorite-stable type with polyacrylate and polymethacrylate being most preferred. The polymer should be of a purity such that it contains a minimum of unsaturated monomers, chemically reactive initiators, terminators, or surfactants present which will hasten the rate of hypochlorite decomposition. The polymer may be present in the formula from 0.05 to 10 wt%, preferably 0.1-0.5 wt%.

Clays such as hectorites and montmorillonites may be included in the compositions of the invention. These constitute a second, separate discontinuous phase from the sequestrant particles. They assist in reduction of spot formation on glassware, and may be present at from 0.3 to 20 wt%. Particularly preferred is the addition of laponite clay at 0.5-2 wt%. An increase in solids level implies a need for lower levels of stabiliser to achieve stability.

Clay may also be incorporated in such amounts so as to provide a thickening effect (see Colgate's GB 2 164 350).

The product has been shown to possess a high degree of stability at room temperature, whilst also demonstrating a suitably low viscosity to assist dispensing. The pH of the composition may range from 10-14, preferably 10.5-12.5. It also demonstrates an improved washing performance in comparison to other thickened machine dishwashing systems.

The liquid detergent composition of the invention may be adapted for use in fabric washing and may further contain any of the adjuncts normally used in fabric washing detergent compositions, eg sequestering agents such as ethylene diamine tetraacetate; alkali silicates for adjusting the pH; soil suspending and anti-redeposition agents such as sodium carboxymethylcellulose, polyvinylpyrrolidone etc; fluorescent agents; perfumes, germicides and colourants.

Further, the addition of lather depressors such as silicones; and enzymes, particularly proteolytic and amylolytic enzymes; and peroxygen or chlorine bleaches, such as sodium perborate and potassium dichlorocyanurate, including bleach activators, such as N,N,N′,N′-tetraacetyl ethylene diamine, may be necessary to formulate a complete heavy duty detergent composition suitable for use in washing machine operations.

Particularly preferred are stable thixotropic liquid machine dishwashing compositions comprising 20-30 wt % of an alkaline metal phosphate, 20-30 wt % of an alkaline metal silicate, 0.1 to 0.5 wt % of a detergent active and water, said compositions further comprising 7 to 11 vol % of air of a particle size as hereinbefore defined according to the invention.

It is preferred that the dishwashing composition has a viscosity at $0.9s^{-1}$ of 20-30 PaS and at $20s^{-1}$ of 2-3 PaS.

It is particularly preferred that said composition has a density of 1.4 to 1.5 g/cm^3.

A further aspect of the present invention is the process for stabilising the composition with a liquid continuous and one or more discontinuous phases. The process comprises aerating the composition with a gas up to 1 to 20% by volume, the gas being present in bubbles size 3-150 microns with average diameter of 3-45 microns. The aeration may be performed during mixing of the composition or afterwards. Depending on the identity and viscosity of the final composition, it may be preferred to aerate during composition mixing. Thus, the difficulty of aerating a viscous liquid and the corrosion of equipment from aerating a highly alkaline composition may be avoided.

If aeration is to be performed during mixing, care must be taken to avoid introducing gas into a phase which will not retain it. For example, pure water will not retain the bubbles in the range 1-150 microns. Most bubbles will quickly migrate to the surface. Usually not until a substantial amount of composition components have been added will water (or any other liquid continuous phases) retain bubbles.

Thus, in mixing a thixotropic cleaning composition as described above, aeration should not start until after addition of the STP or other builder. However, because the builder is the major part of the discontinuous phase, the composition becomes increasingly viscous as more builder is added. Thus, aeration should be stopped after about 50% of the builder is added, the composition being too viscous to aerate by means of mixing equipment beyond that point.

The order of addition of components therefore affects when aeration may occur in the mixing of compositions.

When aeration is performed during mixing the components, it is usually performed by agitation of the composition components. This agitation may be part of blending the components, as by rotating a mixer blade at a speed which entrains air. Suitable devices for aerating the composition include mixing tanks with a stirring blade, turbines, or impellers. The mixing tank may have a closed or open top. Alternatively, other mixers such as a cavity transfer mixer described in International Patent Application WO 83/03222 (Rubber and Plastics Research Association) may be used to aerate. When agitation by these means alone is practised, it is found that the size of air bubbles entrained covers quite a large range, from less than 1 micron to over 1 centimetre. Rather than take more time to agitate the fluid and incorporate sufficient numbers of bubbles of suitable size, it has been found that after limited agitation, the composition or composition components may be circulated through a circulation loop. A circulation loop breaks down all bubbles to a size less than 150 microns. Thus, aeration by agitation and passage through a circulation loop is preferred, as it requires less time and puts more of the entrained air into the desired bubble size.

Although agitation may be the simplest process of aerating, agitation does have drawbacks. One major drawback is the difficulty of incorporating a uniform amount of air into a series of compositions. There is also difficulty in obtaining equal aeration from one machine to another.

Applicants have discovered two alternative means to aerate which overcome this drawback. First, the composition may be mixed without agitation, then charged while under pressure with gas. If the gas added to the composition is dispersed through one or more orifices of diameter 1-150 microns, the size of bubbles dispersed through the composition should also be about 1-150 microns. The advantage of this means of aerating is that more exact amounts of gas may be added to the composition under the more controlled conditions. The result is greater reproducibility of the amount of air added from batch to batch.

Alternatively, the compositions may be aerated to an excess level, ie to a point where the density of the one or more discontinuous phases is less than 85% of the density of the continuous phase. This aeration to excess may be performed either by agitation or addition of gas under pressure. Next, a controled de-aeration takes place by subjecting the composition to a lowered air pressure (eg, lower than 0.2 atmospheres). This lowered pressure will remove some of the gas in the composition. This process of controlled de-aeration has the same benefits as the controlled aeration method.

The invention may be illustrated by the following Examples:

Example 1

A thixotropic machine dishwashing composition was prepared according to the following formulation:

Ingredient	Wt %
Sodium Tripolyphosphate	24.5
Sodum Disilicate	23.0
Na OH	2.0
Av Cl_2	1.2
Stearyl Phosphate	0.2
Sodium Alkyl Sulphonate	0.2
Water	to 100.0

The mixing procedure was as follows:

A premix of water, NaOH, SAS and stearyl phosphate was prepared at 75° and held in a side tank. In a main paddle mixing tank was mixed, at ambient temperature, water (10%), disilicate (48% of a 50% solution), Na OH (4% of a 50% soluton), hypochlorite (8% of a 15% solution). The premix solution was added at 35 °C and the mixing tip speed increased from $1.5ms^{-1}$ to $3ms^{-1}$. The temperature was raised to 50 °C and the STP (Thermphos NW ex Hoechst) added. The mixing speed was raised to $4ms^{-1}$. The mixing continued until a homogenous product was formed and whilst the produced was cooled to 25 °C.

Various product parameters were measured:

Viscosity at $0.9s^{-1}$	25000 mPaS
Viscosity at 20 s^{-1}	2500 mPaS
Phase separation (3 month at RTP)	0 vol%
Density (g/ml)	1.44
pH	13.3
Volume of air incorporated	8 vol%

A microscopic analysis was made of air bubbles in the compositions:

Particle Size (μm)	Percentage (by number)
3-10	32
10-20	42
20-30	15
30-40	3
40-60	3
60-100	3
100-150	2
>150	0

In order to check the washing efficacy of compositions according to the present invention formulated as machine dishwashing liquids, spot, film and cleaning tests were carried out using the above prepared composition.

The liquid was used in a Miele G560 machine on a 65°C programme. A standard set of dishware, soiled with a standard evaluation soil was cleaned ten times, using tap water of 8° German hardness, without using a water softener or a rinse aid. Dosage was 2g/l.

Film and spot formation were assessed visually according to the following scale:

Film Formation	Spot Formation
1 = No film	1 = No spots
2 = Light film	2 = 1-5 spots
3 = Clear film	3 = 6-10 spots
4 = Thick film	4 = 11-20 spots

ASTM test D3556, incorporated herein by reference was also used.

The liquid scored:

Spot	2.4 (glasses)	3.4 (knives)
Film	2.0 (glasses)	2.7 (knives)
ASTM	2.4	

These results are acceptable and show washing to a satisfactory degree.

Examples 2 and 3

A basic detergent composition was formulated according to the procedure of Example 1:

	Wt %
Sodium Tripolyphosphate	24.5
Disilicate (2.0)	23.0
Na OH	2.0
Av Cl_2	1.0
Water	to 100.0

with the addition of various actives. Density and phase separation was measured.

Actives	A	2	3
SAS	-	0.1	-
PAS	-	-	0.1
Stearyl Phosphate	-	0.1	0.1
Density (g/cm^3)	1.547	1.453	1.447
pH	13.8	13.8	13.8
Separation (vol%) - 3 weeks			
37°C	5	1	0
RT	1	0	0
3°C	0	0	0

The Examples show that there is improved physical stability when air is retained (lower density) and that this is due to incorporation of active. Comparative Example A could not be made with a lower density.

Examples 4-7

Following the procedure of Example 1, the following formulations were prepared. Liquid density, phase separation and percentage of air in each formulation was measured.

Ingredient (Wt %)	4	5	6	7
STP	23.50	23.50	24.00	26.00
Silicate	19.00	19.00	22.00	19.00
Na OH	2.00	2.00	2.00	2.50
SAS	0.20	0.20	0.20	0.20
Stearyl Phosphate	0.25	0.16	0.25	0.26
Cl_2	1.20	1.20	1.20	1.00
Water	------------ to 100 ------------			
Liquid Density (g/ml)	1.33	1.44	1.46	1.53
% Air (vol)	12.30	9.90	7.80	1.40
Phase Separation (4 weeks, 37°C)*	-8	0	0	+8

- = bottom separation
+ = top separation

A density difference (D) was measured:

D + density (liquid phase) - density (STP + air) = density (disperse phase)

Calc D	-0.13	0.01	0.04	0.50

Claims

1. A liquid detergent composition comprising:
    (a) from about 5 to 40 wt % of a particulate detergent builder;
    (b) a liquid continuous phase;
    (c) a surface active agent; and
    (d) from about 1 to 20% by volume of a gas present as bubbles ranging in diameter from 3-150 microns and having an average diameter from 3-45 microns;
    the overall density of the composition being from 85% to 115% of the density of the liquid continuous phase alone.

2. A composition as claimed in claim 1 wherein the builder is an alkali metal phosphate.

3. A composition as claimed in claim 1 or claim 2 wherein the liquid continuous phase is aqueous.

4. A composition as claimed in any one of the preceding claims wherein the gas is a noble gas, oxygen, nitrogen, air, halogenated hydrocarbon, carbon dioxide or a mixture thereof.

5. A composition as claimed in any one of the preceding claims wherein at least 90% of the bubbles of gas have a diameter of from 3 to 45 microns.

6. A composition as claimed in any one of the preceding claims wherein the surfactant is present at from 0.05 to 0.4 wt %.

7. An aqueous detergent composition as claimed in any one of the preceding claims having a viscosity of between 5-50 PaS at $0.9s^{-1}$ and 500-5000m PaS at $20s^{-1}$.

8. An aqueous thixotropic liquid detergent composition comprising:
(a) 20-30 wt % of an alkali-metal silicate;
(b) 20-30 wt % of an alkali metal phosphate;
(c) an aqueous liquid continuous phase;
(d) a surface active agent;
(e) 0.1-0.5 wt % of an alkyl phosphate; and
(f) 7-11 vol % of a gas present as bubbles ranging in diameter from 3 to 150 microns and having an average diameter from 3-45 microns;
the overall density of the composition being from 85 to 115% of the density of the aqueous phase alone.

9. A composition as claimed in claim 8 having a viscosity of 20-30 PaS at $0.9s^{-1}$ and 2-3 Pas at $20s^{-1}$.

10. A composition as claimed in claim 8 or claim 9 having a density of 1.4 to 1.5 g/cm^3.

11. A composition as claimed in any one of the preceding claims which yields no more than 2% by volume phase separation at 37°C for 21 days from the time of preparation.

12. A composition as claimed in any one of the preceding claims wherein the particulate detergent builder has a particle size of less than 5 microns when suspended in the aqueous medium.

13. A process for preparing a composition as claimed in any one of the preceding claims wherein the gas is incorporated by a shear mixer.

14. A process as claimed in claim 13 wherein the particulate builder is added as a final step in the preparation.

15. A method of washing dishes in a machine dishwasher with an aqueous medium containing an effective amount of a composition as claimed in any one of claims 1 to 12.

Patentansprüche

1. Flüssige Waschmittelzusammensetzung umfassend:
(a) etwa 5 bis 40 Gew.-% eines teilchenförmigen Waschmittelbuilders;
(b) eine flüssige kontinuierliche Phase;
(c) ein Tensid; und
(d) etwa 1 bis 20 Vol.-% eines Gases, vorliegend in Blasenform mit einem Durchmesser im Bereich von 3 bis 150 µm und mit einem durchschnittlichen Durchmesser von 3 bis 45 µm;
wobei die Gesamtdichte der Zusammensetzung 85 bis 115 % der Dichte der flüssigen kontinuierlichen Phase allein beträgt.

2. Mittel nach Anspruch 1, wobei der Builder ein Alkalimetallphosphat ist.

3. Mittel nach Anspruch 1 oder 2, wobei die flüssige kontinuierliche Phase wässerig ist.

4. Mittel nach einem der vorangehenden Ansprüche, wobei das Gas ein Edelgas, Sauerstoff, Stickstoff, Luft, halogenierter Kohlenwasserstoff, Kohlendioxid oder ein Gemisch davon ist.

5. Mittel nach einem der vorangehenden Ansprüche, wobei mindestens 90 % der Gasblasen einen Durchmesser von 3 bis 45 µm aufweisen.

6. Mittel nach einem der vorangehenden Ansprüche, wobei das Tensid in einer Menge von 0,05-0,4 Gew.-% vorliegt.

7. Wässerige Waschmittelzusammensetzung nach einem der vorangehenden Ansprüche mit einer Viskosität zwischen 5-50 Pas bei 0,9 s^{-1} und 500-5000 mPas bei 20 s^{-1}.

8. Wässerige thixotrope flüssige Waschmittelzusammensetzung, umfassend:
   (a) 20-30 Gew.-% eines Alkalimetallsilicats;
   (b) 20-30 Gew.-% eines Alkalimetallphosphats;
   (c) eine wässerige flüssige kontinuierliche Phase;
   (d) ein Tensid;
   (e) 0,1-0,5 Gew.-% eines Alkylphosphats; und
   (f) 7-11 Vol.-% eines Gases, das als Blasen mit einem Durchmesser im Bereich von 3 bis 150 µm vorliegt, die einen durchschnittlichen Durchmesser von 3 bis 45 µm aufweisen;
   wobei die Gesamtdichte des Mittels 85-115 % der Dichte der wässerigen Phase allein beträgt.

9. Mittel nach Anspruch 8 mit einer Viskosität von 20-30 Pas bei 0,9 s^{-1} und 2-3 Pas bei 20 s^{-1}.

10. Mittel nach Anspruch 8 oder 9 mit einer Dichte von 1,4 bis 1,5 g/cm^3.

11. Mittel nach einem der vorangehenden Ansprüche, das nicht mehr als 2 Vol.-% Phasentrennung bei 37 °C für 21 Tage vom Zeitpunkt der Herstellung an aufweist.

12. Mittel nach einem der vorangehenden Ansprüche, wobei der teilchenförmige Waschmittelbuilder eine Teilchengröße von weniger als 5 µm aufweist, wenn er in dem wässerigen Medium suspendiert ist.

13. Verfahren zur Herstellung eines Mittels nach einem der vorangehenden Ansprüche, wobei das Gas mit einem Scherwirkung-ausübenden Mischer eingebracht wird.

14. Verfahren nach Anspruch 13, wobei der teilchenförmige Builder in einem letztlichen Schritt bei der Herstellung zugeführt wird.

15. Verfahren zum Geschirrwaschen in einer Geschirrwaschmaschine mit einem wässerigen Medium, das eine wirksame Menge eines Mittels nach einem der Ansprüche 1 bis 12 enthält.

Revendications

1. Composition détergente liquide, qui comprend :
   (a) environ 5 à 40% en poids d'un adjuvant détergent particulaire ;
   (b) une phase liquide continue ;
   (c) un agent tensioactif ; et
   (d) environ 1 à 20% en volume d'un gaz présent sous forme de bulles dont le diamètre est compris entre 3 et 150 µm et dont le diamètre moyen est de 3 à 45 µm ;
   la densité globale de la composition étant de 85 à 115% de la densité de la phase liquide continue seule.

2. Composition selon la revendication 1, dans laquelle l'adjuvant est un phosphate de métal alcalin.

3. Composition selon la revendication 1 ou 2, dans laquelle la phase liquide continue est aqueuse.

4. Composition selon l'une quelconque des revendications précédentes, dans laquelle le gaz est un gaz noble, l'oxygène, l'azote, l'air, un hydrocarbure halogéné, l'anhydride carbonique ou un mélange de ceux-ci.

5. Composition selon l'une quelconque des revendications précédentes, dans laquelle au moins 90% des bulles gazeuses ont un diamètre de 3 à 45 µm.

6. Composition selon l'une quelconque des revendications précédentes, dans laquelle le tensioactif est présent à raison de 0,05 à 0,4% en poids.

7. Composition détergente aqueuse selon l'une quelconque des revendications précédentes, présentant une viscosité comprise entre 5 et 50 Pa.s à 0,9 s^{-1} et entre 500 et 5000 mPa.s à 20 s^{-1}.

8. Composition détergente liquide aqueuse thixotropique, qui comprend :
(a) 20 à 30% en poids d'un silicate de métal alcalin ;
(b) 20 à 30% en poids d'un phosphate de métal alcalin ;
(c) une phase liquide aqueuse continue ;
(d) un agent tensioactif ;
(e) de 0,1 à 0,5% en poids d'un alkylphosphate ; et
(f) de 7 à 11% en volume d'un gaz sous forme de bulles dont les diamètres sont compris entre 3 et 150 μm et dont le diamètre moyen est de 3 à 45 μm ;
la densité globale de la composition étant de 85 à 115% de la densité de la phase aqueuse seule.

9. Composition selon la revendication 8, dont la viscosité est de 20 à 30 Pa.s à 0,9 s^{-1} et de 2 à 3 Pa.s à 20 s^{-1}.

10. Composition selon la revendication 8 ou 9, ayant une densité de 1,4 à 1,5 g/cm^3.

11. Composition selon l'une quelconque des revendications précédentes, qui ne produit pas plus de 2% de séparation de phases en volume à 37 ° C pendant 21 jours à partir du moment de sa préparation.

12. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'adjuvant détergent particulaire présente une granulométrie inférieure à 5 μm, quand il est en suspension dans le milieu aqueux.

13. Procédé de préparation d'une composition selon l'une quelconque des revendications précédentes, dans lequel on incorpore le gaz à l'aide d'un mélangeur à cisaillement.

14. Procédé selon la revendication 13, dans lequel on ajoute l'adjuvant particulaire en un stade final de la préparation.

15. Procédé de lavage de vaisselle en machine avec un milieu aqueux qui contient une proportion efficace d'une composition selon l'une quelconque des revendications 1 à 12.