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(54) **Abrasive-containing liquid detergent compositions and non-clogging dispensing package therefor.**

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Abrasive-containing liquid detergent compositions and non-clogging dispensing package therefor

Background

The invention relates to liquid detergent compositions containing specified amounts and types of insoluble abrasives which are especially useful in the washing of dishes. The compositions contain high-sudsing surfactants and may also contain detergency builders which complement the action of the
5 abrasive.

The invention also relates to the combination of such liquid detergents and a package which provides convenient dispensing of the detergent composition without clogging.

The use of abrasives in powdered scouring cleansers is well known. Scouring cleansers generally contain a relatively high level of abrasive. When such scouring cleansers are used as adjuncts in the
10 dishwashing process such products provide abracing power to make the removal of cooked, burnt or dried-on foods on kitchenware easier and more convenient. Recently, liquid scouring cleansers containing water-insoluble abrasives have become available. Such liquid compositions are disclosed in U.S. Patents 3,149,078; 3,210,285; 3,210,286; 3,214,380; 3,579,456; 3,623,990; 3,677,954; 3,813,349; 3,966,432; and 4,129,527; and British Patents 1,384,244 and 1,534,680. The use of
15 scouring cleansers, however, is normally in addition to a specific dishwashing product, one product being required for removal of non-sticking soils, especially fats and oils, and a second product being required for scouring purposes. Canadian Patent 1,048,365 discloses granular detergent compositions suitable for dishwashing containing 20% to 35% surfactant and 5% to 20% of abrasive material having a particle diameter in the range of 200 to 850 micrometers.

It is an object of the present invention to provide liquid detergent compositions containing a surfactant and an abrasive, the detergent composition being highly effective in removing food soils from kitchenware when used undiluted or in the form of a relatively concentrated water slurry, but which is highly acceptable for hand dishwashing in the dilute water solutions typically used with liquid dishwashing products.

It is a further object of the present invention to provide liquid detergent compositions containing a surfactant and an abrasive in a non-clogging dispensing package, the detergent composition being highly effective in removing food soils from kitchenware when used undiluted or in the form of a relatively concentrated water slurry, but which in a preferred embodiment is acceptable for hand dishwashing in the dilute water solutions typically used with liquid dishwashing products. It is a further object to
30 provide a package suitable for such a product.

Summary of the invention

The present invention comprises a liquid detergent composition containing by weight:

- 35 a) from 20% to 35% of an anionic surfactant;
b) from 2% to 15% of a suds stabilizing nonionic surfactant selected from amine oxides, amides, and the ethylene oxide condensates of alcohols and alkyl phenols;
c) from 1% to 20% of a water-insoluble abrasive having a particle diameter of from 15 to 150 micrometers and a hardness on the Mohs scale of from 2 to 7; and
40 d) from 20% to 75% water; said composition providing an initial suds cover to a dishwashing solution and a suds cover after the washing of eight plates when used at a concentration of 0.07% in 7.57 litres of 46°C water containing 120 mg/l water hardness measured as CaCO₃, each plate carrying 4.0 ml. of triglyceride-containing soil.

45 The essential package characteristics are:

- a) a flexible plastic container adapted to provide an increase in internal pressure by application of compressive forces to one or more external surface areas, and
b) a clog resistant dispensing closure adapted to be mounted on said flexible plastic container, said
50 closure consisting of a body portion and a bail-like sealing member, the body portion consisting of an annular skirt for surrounding said container finish, means for attaching said skirt to said container finish and a domed nozzle section with a central aperture, said aperture having an horizontal cross sectional area from 1.29 mm² to 16.13 mm², preferably from 3.23 mm²—9.67 mm², a minimum diameter of 0.127 cm preferably 0.20 cm, and a length of no more than 0.635
55 cm, said bail-like sealing member having an arcuate conformation and a rotatable joint to said body section at each end, said sealing member having a gripping portion centrally located and a downwardly-projecting protrusion on its underside adapted to plug the outside of said aperture when the sealing member is in a closed position.

60 **Detailed description of the invention**

The detergent compositions of the present invention contain three essential components:

- a) a surfactant

- b) a water-insoluble abrasive
c) water.

Optional ingredients can be added to provide various performance and aesthetic characteristics.

5 Surfactant

The compositions of this invention contain from 20% to 35% of an anionic surfactant or mixtures thereof.

Many anionic detergents can be broadly described as the water-soluble salts, particularly the alkali metal, alkaline earth metal, ammonium and amine salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from 8 to 22 carbon atoms and a radical selected from sulfonic acid and sulfuric acid ester radicals. Included in the term alkyl is the alkyl portion of high acyl radicals. Examples of the anionic synthetic detergents which can form the surfactant component of the compositions of the present invention are the sodium, ammonium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 — C_{18} carbon atoms) sodium or potassium alkyl benzene or toluene sulfonates, in which the alkyl group contains from 9 to 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); sodium or potassium paraffin sulfonates and olefin sulfonates in which the alkyl or alkenyl group contains from 10 to 20 carbon atoms; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with 1 to 30 units of ethylene oxide per molecule and in which the radicals contain from 3 to 12 carbon atoms; the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil and sodium or potassium beta-acetoxy- or beta-acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

Specific examples of alkyl sulfate salts which can be employed in the instant detergent compositions include sodium lauryl alkyl sulfate, sodium stearyl alkyl sulfate, sodium palmityl alkyl sulfate, sodium decyl sulfate, sodium myristyl alkyl sulfate, potassium lauryl alkyl sulfate, potassium stearyl alkyl sulfate, potassium decyl sulfate, potassium palmityl alkyl sulfate, potassium myristyl alkyl sulfate, sodium dodecyl sulfate, potassium dodecyl sulfate, potassium tallow alkyl sulfate, sodium tallow alkyl sulfate, sodium coconut alkyl sulfate, potassium coconut alkyl sulfate and mixtures of these surfactants. Highly preferred alkyl sulfates are sodium coconut alkyl sulfate, potassium coconut alkyl sulfate, potassium lauryl alkyl sulfate and sodium lauryl alkyl sulfate.

Suitable alkylbenzene or alkyltoluene sulfonates include the alkali metal (lithium, sodium, potassium), alkaline earth (calcium, magnesium) and alkanolamine salts of straight-or branched-chain alkylbenzene or alkyltoluene sulfonic acids. Alkylbenzene sulfonic acids useful as precursors for these surfactants include decyl benzene sulfonic acid, undecyl benzene sulfonic acid, dodecyl benzene sulfonic acid, tridecyl benzene sulfonic acid, tetrapropylene benzene sulfonic acid. Preferred sulfonic acids as precursors of the alkyl-benzene sulfonates useful for compositions herein are those in which the alkyl chain is linear and averages about 12 carbon atoms in length. Examples of commercially available alkyl benzene sulfonic acids useful in the present invention include Conoco SA 515 and SA 597 marketed by the Continental Oil Company and Calsoft LAS 99 marketed by the Pilot Chemical Company.

Particularly preferred anionic surfactants useful herein are alkyl ether sulfates having the formula $RO(C_2H_4O)_xSO_3M$ wherein R is alkyl or alkenyl of 10 to 20 carbon atoms, x is 1 to 30, and M is a water-soluble cation. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having from 10 to 20 carbon atoms. Preferably, R has 12 to 18 carbon atoms. The alcohols can be derived from natural fats, e.g., coconut oil or tallow, or can be synthetic. Such alcohols are reacted with 1 to 30, and especially 1 to 12, molar proportions of ethylene oxide and the resulting mixture of molecular species is sulfated and neutralized.

Specific examples of alkyl ether sulfates of the present invention are sodium coconut alkyl triethylene glycol ether sulfate, magnesium tallow alkyl triethylene glycol ether sulfate, and sodium tallow alkyl hexaoxy ethylene sulfate. Preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from 12 to 16 carbon atoms and an average degree of ethoxylation of from 1 to 12 moles of ethylene oxide.

Additional examples of anionic surfactants useful herein are the compounds which contain two anionic functional groups. These are referred to as di-anionic surfactants. Suitable dianionic surfactants are the disulfonates, disulfates, or mixtures thereof which may be represented by the following formula:



where R is an acyclic aliphatic hydrocarbyl group having 15 to 20 carbon atoms and M is a water-solubilizing cation, for example, the C_{15} to C_{20} disodium 1,2-alkyldisulfates, C_{15} to C_{20} dipotassium-1,2-alkyldisulfonates or disulfates, di-sodium 1,9-hexadecyl disulfates, C_{15} to C_{20} disodium 1,2-alkyl-disulfonates, disodium 1,9-stearyldisulfates and 6,10-octadecyldisulfates.

Nonionic surfactant

The compositions of this invention contain from 2% to 15%, preferably from 3% to 8%, most preferably 4%, of a suds stabilizing nonionic surfactant or mixtures thereof. The presence of this component is essential to satisfactory performance and acceptance as a complete dishwashing
 5 product. In preferred embodiments the nonionic surfactant will be in a weight ratio to the anionic surfactants of from 1:10 to 1:2, most preferably from 1:7 to 1:3.

Nonionic surface active agents operable in the instant compositions can be any of three basic types—the alkylene oxide condensates, the amides and the semi-polar nonionics.

The alkylene oxide condensates are broadly defined as compounds produced by the condensation
 10 of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which can be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of such alkylene oxide condensates include:

15 (1) The condensation products of aliphatic alcohols with ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched and generally contains from 8 to 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of 6 moles of ethylene oxide with 1 mole of tridecanol, myristyl alcohol condensed with 10 moles of ethylene oxide per mole of myristyl alcohol, the condensation product of ethylene oxide with coconut fatty alcohol wherein the
 20 coconut alcohol is a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms and wherein the condensate contains 6 moles of ethylene oxide per mole of alcohol, and the condensation product of 9 moles of ethylene oxide with the above-described coconut alcohol. An example of a commercially available non-ionic surfactant of this type includes Neodol (23—6.5 marketed by the Shell Chemical Company.

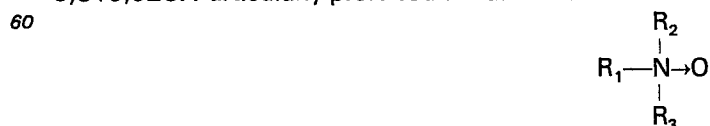
25 (2) The polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for example, from polymerized propylene, diiso-
 30 butylene, octene, or nonene. Examples of compounds of this type include nonyl phenol condensed with 9.5 moles of ethylene oxide per mole of nonyl phenol, dodecyl phenol condensed with 12 moles of ethylene oxide per mole of phenol, dinonyl phenol condensed with 15 moles of ethylene oxide per mole of phenol, di-isooctylphenol condensed with 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO—610 marketed by the GAF
 35 Corporation; and Triton X—45, X—114, X—100 and X—102, all marketed by the Rohm and Haas Company.

(3) The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds has a molecular weight of from 1500 to 1800 and of course exhibits water insolubility. The addition of
 40 polyoxyethylene moieties to this hydrophobic portion tends to increase the water-solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product. Examples of compounds of this type include certain of the commercially available Pluronic surfactants marketed by the Wyandotte Chemicals Corporation.

45 (4) The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. The hydrophobic base of these products consists of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of from 2500 to 3000. This base is condensed with ethylene oxide to the extent that the condensation product contains from 40% to 80% by weight of polyoxyethylene and has a molecular weight of from 5,000 to
 50 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic compounds marketed by the Wyandotte Chemicals Corporation.

Examples of the amide type of nonionic surface active agent include the ammonia, monoethanol and diethanol amides of fatty acids having an acyl moiety of from 8 to 18 carbon atoms. These acyl moieties are normally derived from naturally occurring glycerides, e.g., coconut oil, palm oil, soybean oil
 55 and tallow, but can be derived synthetically, e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process.

Examples of the semi-polar type of nonionic surface active agents are the amine oxides, phosphine oxides and sulfoxides. These materials are described more fully in Berry, U.S. Patent 3,819,528. Particularly preferred are amine oxides of the formula:



65 wherein R_1 is a C_{10-18} alkyl and R_2 and R_3 are methyl or ethyl.

The level and type of surfactant used in the compositions of this invention provide an initial suds cover to a dishwashing solution and a suds cover after the washing of 8 plates when used at a concentration of 0.07% in 7.57 litres of 46°C water containing 120 mg/l water hardness measured as CaCO_3 , each plate carrying 4.0 ml of a triglyceride containing soil. Suds are generated by mechanical agitation and the suds cover and height measured. A dinner plate carrying the soil is washed successively with the introduction of 4.0 ml of soil each time. An essentially complete suds cover of the washing solution is more important than suds height, but, preferably, the suds cover after the washing of 8 plates is at least 1.27 cm in height.

The sudsing characteristic of the preferred high-sudsing compositions of the invention is that necessary to provide the user of the product with an indication of cleaning potential in a dishwashing solution. Soils encountered in dishwashing act as suds depressants and the presence or absence of suds from the surface of a dishwashing solution is a convenient guide to product usage. Mixtures of anionic surfactants and nonionic surfactants, especially amides and amine oxide nonionic surfactants, are utilized in the compositions of the invention because of their high sudsing characteristics, their suds stability in the presence of food soils and their ability to indicate accurately an adequate level of product usage in the presence of soil.

Optional surfactants

The compositions of the invention may contain optional surfactants other than anionic and nonionic surfactants such as ampholytic, zwitterionic and cationic surfactants.

Ampholytic surfactants can be broadly described as derivatives of aliphatic amines which contain a long chain of 8 to 18 carbon atoms and an anionic water-solubilizing group, e.g. carboxy, sulfo or sulfate. Examples of compounds falling within this definition are sodium-3-dodecylamino propane sulfonate, and dodecyl dimethylammonium hexanoate.

Zwitterionic surface active agents operable in the instant composition are broadly described as internally-neutralized derivatives of aliphatic quaternary ammonium and phosphonium and tertiary sulfonium compounds in which the aliphatic radical can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono.

Cationic surfactants such as quaternary ammonium compounds can find optional use in the practice of the invention to the extent they are compatible with the other surfactants in the particular composition.

Abrasive

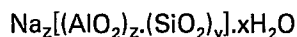
The abrasive agent can be any of the water-insoluble abrasive materials known in the art which have a particle diameter of from 15 to 150, preferably from 35 to 125, microns and a hardness on the Mohs scale of from 2 to 7. Included are materials such as a gate, mica, calcite, garnet, quartz, kieselguhr, silica, marble, tripoli, flint, feldspar, emery, pumice, alumina, perlite, expanded perlite, volcanic ash, diatomaceous earth, bentonite, amorphous silica from dehydrated silica gels, precipitated silica, plastics such as polystyrene and polyacrylates, and natural and synthetic aluminosilicates and mixtures thereof.

The amount of abrasive included in the compositions is in the range of from 1% to 20% of the total composition by weight. Preferred compositions contain from 5% to 10% by weight of abrasive.

Optional detergency builder

The compositions of this invention can contain up to 20%, preferably from 5% to 15%, by weight of detergency builders either of the organic or inorganic types. Examples of water-soluble inorganic builders which can be used, alone or in admixture with themselves and organic alkaline sequestrant builder salts, are alkali metal carbonates, polyphosphates, and silicates. Specific examples of such salts are sodium tripolyphosphate, sodium carbonate, potassium carbonate, sodium pyrophosphate, potassium pyrophosphate, potassium tripolyphosphate, and sodium hexametaphosphate. Examples of organic builder salts which can be used alone, or in admixture with each other or with the preceding inorganic alkaline builder salts, are alkali metal polycarboxylates, e.g., water-soluble citrates such as sodium and potassium citrate, sodium and potassium tartrate, sodium and potassium ethylene-diaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-ethylene diamine triacetates, sodium and potassium nitrilo triacetates (NTA) and sodium and potassium N-(2-hydroxyethyl)-nitrilo diacetates. Other organic builder salts include the alkali metal salts of phytic acid, e.g., sodium phytate (see U.S. Patent 2,739,942). Water-soluble salts of ethane-1-hydroxy-1,1-diphosphonate (EHDP) are also suitable. Mixtures of any of the preceding water-soluble organic or inorganic builder salts can be used.

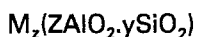
The compositions of this invention can contain insoluble builder salts selected from certain zeolites or aluminosilicates. One such aluminosilicate which is useful in the compositions of the invention is water-insoluble crystalline aluminosilicate ion exchange material of the formula:



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wherein Z and y are at least 6, the molar ratio of Z to y is from 1.0 to 0.5 and x is from 10 to 264, said material having a particle size diameter of from 0.1 micrometer to 10 micrometers, a calcium ion exchange capacity of at least 200 mg. CaCO₃ eq./gram and a calcium ion exchange rate of at least 34.1 mg Ca⁺⁺/litre/minute/gram. This ion exchange builder is more fully described in Belgian Patent 814,874. A preferred aluminosilicate of this type is Zeolite A.

A second water-insoluble aluminosilicate ion exchange material useful herein is water-insoluble amorphous hydrated aluminosilicate material of the empirical formula:



wherein M is sodium, potassium, ammonium, or substituted ammonium, Z is from 0.5 to 2, y is 1 and said material having a particle size diameter of less than 100, preferably less than 10 micrometers, a magnesium ion exchange capacity of at least 50 milligrams equivalent of CaCO₃ hardness per gram of anhydrous aluminosilicate and a Mg⁺⁺ exchange rate of at least 17.1 mg/liter/minute/gram/liter; and mixtures thereof. This ion exchange builder is more fully described in Gedge et al's French Patent 2,237,839.

Water

The compositions of this invention contain from 20% to 75% water.

Optional ingredients

Alcohols, such as ethyl alcohol, and hydrotropes, such as sodium and potassium toluene sulfonate, sodium and potassium xylene sulfonate, trisodium sulfosuccinate and related compounds (as disclosed in U.S. Patent 3,915,903), and urea, can be utilized in the interests of achieving a desired product phase stability, viscosity, and yield value. Also useful in the compositions of this invention are suspending or thickening agents such as those disclosed in U.S. Patent 3,393,153 including colloidal silica having a mean particle diameter ranging from 0.01 micrometers to 0.05 micrometers colloidal clays such as bentonites or chemically treated bentonites, isomorphous silicates, especially those with a high magnesium content, and particulate polymers such as polystyrene, oxidized polystyrene having an acid number of from 20 to 40, sulfonate polystyrene having an acid number of from 10 to 30, polyethylene, oxidized polyethylene having an acid number of from 10 to 30; sulfonated polyethylene having an acid number of from 5 to 25; polypropylene, oxidized polypropylene having an acid number of from 10 to 30 and sulfonated polypropylene having an acid number of from 5 to 25, all of said particulate polymers having mean particle diameters ranging from 0.01 micrometers to 30 micrometers. Other examples of suspending and thickening agents include copolymers of styrene with monomers such as maleic anhydride, nitrilnitrile, methacrylic acid and lower alkyl esters of methacrylic acid, copolymers of styrene with methyl or ethyl acrylate, methyl or ethyl maleate, vinyl acetate, acrylic, maleic or fumaric acids and mixtures thereof. The mole ratio of ester and/or acid to styrene is preferably in the range from 4 to 40 styrene units per ester and/or acid unit. Such materials preferably have a mean particle diameter range of from 0.05 micrometers to 1 micrometer and molecular weights ranging from 500,000 to 2,000,000. Cellulosic polymers such as carboxymethyl cellulose and hydroxypropyl cellulose and gums such as guar gum and gum tragacanth are also suitable suspending and thickening agents.

The detergent compositions of this invention can contain, if desired, any of the usual adjuvants, diluents and additives, for example, perfumes, enzymes, dyes, antitarnishing agents, antimicrobial agents, and the like, without detracting from the advantageous properties of the compositions. Alkalinity sources and pH buffering agents such as alkali metal carbonates and bicarbonates, monoethanolamine, triethanolamine, alkali metal hydroxides, etc., can also be utilized. A preferred pH range for a 1% solution in water is from 6 to 11.

Physical characteristics of the detergent composition

The liquid detergent compositions of the invention contain abrasives as suspended solids and may contain other solid or liquid ingredients that provide desired product stability characteristics and that affect product viscosity. In general, the products of the invention are thixotropic or pseudoplastic and resistant to settling out of the abrasive or other solids yet sufficiently fluid for dispensing with the package of the invention. In general, the compositions have a Brookfield viscosity of from 400 mPas. to 2500 mPas. when measured at 50 rpm and a yield value of from 5 to 600×10⁻⁵M per square centimeter at 25°C.

The important physical property consideration of the compositions of the invention is their yield value. The consistency of simple (or Newtonian) liquids is a function of the nature of the material, temperature, and pressure only. This consistency is known as the "fluid viscosity coefficient", "absolute viscosity," or merely "viscosity", and is usually measured in centipoises (1 centipoise=0.01 gram/centimeter-second). With a Newtonian liquid, any force applied to the system produces some deformation, according to the formula $du/dr = F/\mu$ where du/dr =the rate of shear; F =the shear stress, or shearing force per unit area; and μ =the viscosity coefficient.

In the case of non-Newtonian liquids, on the other hand, the consistency is a function of the material, pressure, temperature, and also the shear stress applied to the system. Those non-Newtonian liquids which are classified as Bingham plastics, or real plastics, are not always deformed when a force is applied to the system. Deformation, if any, takes place according to the formula $du/dr = (F/j)\mu_a$ where

5 μ_a = the apparent viscosity, or plastic viscosity, at the shear stress F ; j = a characteristic of the liquid called the yield stress, or yield value, measured in units of pressure; and du/dr and F are as defined above.

If the shear stress applied to the system is less than the yield value, the system will not be deformed at all. Hence a Bingham plastic system is capable of supporting indefinitely insoluble

10 particulate material which has a density greater than that of the supporting medium, so long as the material has such a particle size and density that the shear stress which each particle places on the supporting medium does not exceed the yield value.

This is to be contrasted with suspension of heavy insoluble particulate material in Newtonian liquids with high viscosities. In highly viscous Newtonian liquids, insoluble particulate material is

15 suspended only because the rate of flow is slow. In Bingham plastics, insoluble particulate material is suspended because the stress imposed by the particles does not exceed the yield value of the liquid, and therefore, there is no flow at all. Of course, if the yield value of the supporting medium should sufficiently decrease for any reason, the particles would not longer be suspended. This could be caused, for example, by a physical or chemical change in the supporting medium. If one of the components of

20 the supporting medium is an emulsion which settles into layers upon standing, the yield value can be lost temporarily, but in such a case, the original composition can be reconstituted by mixing. If a chemical reaction either consumes a vital component or produces a damaging one, the loss of yield value can be permanent.

Because it is usually not known whether a system behaves in a truly plastic manner at low shear

25 rates, the measurement of exact yield values is estimated, in Newtons $\times 10^{-5}$ per square centimeter, by the following relationship:

$$\text{Yield Value} = \frac{\text{Viscosity at 0.5 r.p.m.} - \text{Viscosity at 1 r.p.m.}}{100}$$

30

This relationship represents an extrapolation of the sheer curve to 0 r.p.m. since an absolute shear stress cannot be measured at 0 r.p.m.

The yield value of the liquid detergent compositions of this invention ranges from 5×10^{-5} to

35 600×10^{-5} N per square centimeter. If the yield value is too low, the insoluble, particulate material will not be suspended, because the weight of the individual particles, distributed over the area which supports the particles, will exceed the yield value. However, if the yield value is too great, the composition will become thick and unmanageable because as the yield value increases, so will the apparent viscosity.

40 A preferred range of yield values to support the insoluble particulate material used in the liquid detergent compositions of this invention is from 100×10^{-5} to 400×10^{-5} Newtons per square centimeter.

The physical characteristics of the compositions can present a dispensing problem because of a slow "drain back" characteristic that leads to product retention and subsequent clogging in various

45 parts of a dispensing closure. This difficulty is greatly intensified when the closure is not sealed after use and water and other solvents evaporate from the product retained in the closure.

The clog resistant package

As discussed hereinbefore the essential package elements are: 1) a flexible package container to

50 provide the squeeze dispensing characteristics typical of a variety of consumer products including dishwashing liquids and liquid abrasive cleansers; and 2) a clog resistant closure.

Typical dishwashing liquid detergents have a viscosity within the range of from 30 mPas to 300 mPas, contain no suspended solids other than low levels of opacifiers and are not thixotropic or pseudo-plastic to any great extent. Closure clogging is not a serious problem and directional control of

55 dispensed product is of no particular concern.

As disclosed, for example, in U.S. Patents 3,981,421 and 4,065,037, the design of closures for abrasive liquid cleaning preparations involve consideration of the thixotropic nature of such products because of product retention in the closure aperture.

In the package of the present invention, the closure design is distinguished by elements particularly

60 suited to the dispensing of the product of the invention.

The design elements of particular importance are:

- 1) the absence of internal mechanisms or other obstructions to product flow in the closure up to the aperture;
- 65 2) a domed nozzle portion with a horizontal inner diameter of at least 0.51 cm;

- 3) an aperture through the domed nozzle portion with a horizontal cross sectional area of from 1.29 mm² to 16.13 mm² a minimum diameter of 0.127 cm and a length through the dome wall of no more than 0.635 cm.

5 The domed or hemispherical nozzle design with its absence of actue angles, i.e. "corners" does not allow any appreciable product buildup and has the beneficial effect of concentrating and focusing any compressive force applied to the flexible container in a manner to keep the nozzle region and aperture clear of product buildup. The release of pressure from the container after dispensing clears the aperture.

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Brief description of the drawings

Figure 1 is a top plan view of an example of the closure of the invention.

Figure 2 is a cross sectional view taken along the line 2—2 of Figure 1.

Figure 3 is a partial section, taken along the line 3—3 of Figure 1.

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Description of preferred package embodiments

An example of the dispensing closure of the present invention is illustrated in Figures 1 through 3 wherein like parts are identified by the same number. The closure is generally indicated at 1 having a body portion 2 and a bail-like sealing member 3. The body portion 2 has a downwardly depending annular portion or skirt 4. The inside surface of the annular portion 4 is provided with threads 5 adapted to mate and engage corresponding threads on the neck or finish of a container (not shown). Means other than threading as are well known in the art may be employed to engage the closure 1 with the neck or finish of a container within the scope of the present invention. The outside surface of the annular portion 4 can, if desired, be provided with grooves, ridges or the like both for decorative purposes and to facilitate grasping of the shell for threading it onto the container finish. The interior surface of the top portion of the body portion 2 can have a downwardly depending annual rib 6 to abut and form a seal with the top surface of the container finish.

A chimney 7 is located centrally of the top portion of the body portion 2. The chimney is generally cylindrical in configuration and is provided with an axial bore 8, open at its lower end to communicate with the interior of the container and is surmounted at its upper end with a domed or hemispherical portion 9 terminating in an aperture 10 for dispensing the product from the container and closure. The diameter of the axial bore 8 also defines the interior horizontal diameter of the domed portion which preferably is at least 0.51 cm. The bail-like sealing member 3 has an arcuate conformation and rotatable joints 11, 12 with the top portion of the closure body portion 2. In other embodiments, the joint is located on the outside wall of the chimney by means, for example, of protuberant posts from the chimney engaging sockets on the sealing member. The sealing member 3 has a gripping portion 13 centrally located and a downwardly projecting protrusion 14 adapted to plug the aperture 10 when the sealing member 3 is in an closed position.

The sealing member may be adapted to provide a more positive seal of the protrusion 14 with the aperture 10 during shipment than is desirable during the period of consumer use. By way of example, the posts 15, 16 can be engaged into sockets 17, 18 for shipment and sale.

Although the materials used for the dispensing package portion of the invention can be any materials that meet the stated qualifications, conventional plastic material are generally satisfactory. The container may be made of such materials as polyethylene, polypropylene or polyvinyl chloride. Particularly suitable are materials capable of formation into containers by blow molding. The parts of the closure can be made from plastic materials such as polyethylene, polystyrene, polycarbonates or polypropylene that can be formed into desired shapes by injection molding. Materials resistent to cold flow such as the polycarbonates are particularly suitable for the sealing member.

The following examples are given to illustrate the detergent compositions of the invention. All amounts and percentages are by weight unless otherwise indicated.

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Example I

Liquid detergent compositions were prepared containing the ingredients listed below:

	A	B	C	D	E
5 Sodium C ₁₂₋₁₃ alkyl sulfate	11.5%	11.5%	11.5%	11.5%	11.5%
Sodium C ₁₂₋₁₃ ethoxy (3) alkyl sulfate	12.5	12.5	12.5	12.2	12.5
C ₁₂₋₁₄ alkyl dimethyl amine oxide	4.0	4.0	4.0	4.0	—
10 C ₁₂₋₁₄ alkyl monoethanol-amide	—	—	—	—	6.0
Trisodium sulfosuccinate	2.0	2.0	2.0	3.0	3.0
Calcite (avg. diameter=125 μm)	—	10.0	—	—	—
15 Diatomaceous earth (avg. diameter=60 μm)	5.0	—	—	—	—
Diatomaceous earth (avg. diameter=40 μm)	—	—	—	5.0	5.0
Silica (43—105 μm diameter)	—	—	5.0	—	—
20 Bentonite clay (suspending agent)	2.5	2.5	—	2.2	2.2
Fumed silica (CAB-O-Sil)	—	—	2.0	—	—
Ethanol	10.0	10.0	10.0	10.0	10.0
Water and miscellaneous	—	—	Balance	—	—
25 Viscosity (Brookfield-50 rpm)	1200— 1800 mPas	1200— 1800 mPas	1200— 1800 mPas	1200— 1800 mPas	1200— 1800 mPas
Yield value (10 ⁻⁵ N/cm ²)	250	250	250	250	250

All compositions listed above contain approximately 45 to 55% water and have a pH value in the range of 8.0 to 10.0.

The compositions are entirely satisfactory when used in dilute solutions as a dishwashing detergent compositions and are substantially superior to typical liquid dishwashing detergent compositions when used undiluted or in concentrated solution for removal of tightly attached soils.

Equivalent results are obtained when C₁₂ alkyldiethanolamide and the reaction product of a C₁₂₋₁₅ alcohol and 8 moles of ethylene oxide are substituted for the C₁₂ alkylmonoethanolamide of Composition E.

Equivalent results are obtained when sodium C₁₂₋₁₃ alkylbenzene sulfonate and C₁₂₋₁₅ paraffin sulfonate are substituted for the sodium C₁₂₋₁₃ alkyl sulfate of compositions A, B, C, D and E.

Compositions A and B were stored in packages of the invention with a closure having a circular cross-section aperture with a diameter of 0.305 cm. Product was dispensed from 624 ml containers as packed and after storage of 3, 8, 10, 17 and 30 days. When the aperture was covered between uses, there was essentially no evidence of clogging to restrict or misdirect product flow when the container was subjected to a pressure of 26.65 N applied 10.2 cm from the base of the container. When the aperture was left open between uses, performance was impaired but generally satisfactory. Control samples utilizing the "push-pull" liquid detergent closure of U.S. Patents 3,227,332 and 3,201,013 and the liquid abrasive cleanser closures of U.S. Patents 3,981,421 and 4,065,037 did not provide dispensing characteristics as satisfactory.

Equivalent results are obtained when sodium C₁₂₋₁₃ alkyl benzene sulfonate is substituted for the sodium C₁₂₋₁₃ alkyl sulfate of compositions A, B, C, D and E.

Claims

1. An abrasive-containing liquid detergent composition comprising by weight:

- from 20% to 35% of an anionic surfactant;
- from 2% to 15% of a suds stabilizing nonionic surfactant selected from the group consisting of amine oxides, amides and the ethylene oxide condensates of alcohols and alkyl phenols;
- from 1% to 20% of a water-insoluble abrasive having a particle diameter of from 15 to 150 micrometers and a hardness on the Mohs scale of from 2 to 7; and
- from 20% to 75% water;

said composition providing an initial suds cover to a dishwashing solution and a suds cover after the washing of eight plates when used at a concentration of 0.07% in 7.57 liters of 46°C water containing 120 mg/l water hardness measured as CaCO₃, each plate carrying 4.0 ml. of triglyceride-containing soil.

2. An abrasive-containing liquid detergent composition in a clog-resistant dispensing package comprising:

- (a) an abrasive containing liquid detergent composition according to Claim 1; and
- (b) a clog-resistant package containing said liquid detergent composition comprising:
 - (i) a flexible plastic container adapted to provide an increase in internal pressure by application of a compressive force to one or more external surface areas, and
 - (ii) a clog-resistant dispensing closure adapted to be mounted on said flexible plastic container said closure consisting of a body portion and bail-like sealing member, the body portion consisting of an annular skirt for surrounding said container finish, means for attaching said skirt to said container finish and a domed nozzle section with a central aperture, said aperture having a horizontal cross sectional area from 1.29 mm² to 16.13 mm² a minimum diameter of 0.127 cm and a length of not more than 0.635 cm, said bail-like sealing member having an arcuate conformation and a rotatable joint to said body section at each end, said sealing member having a gripping portion centrally located and a downwardly-projecting protrusion on its underside adapted to plug the outside of said aperture when the sealing member is in closed position.

3. An abrasive-containing liquid detergent according to Claims 1 or 2 wherein the anionic surfactant comprises a material selected from the group consisting of alkyl sulfates, alkyl ether sulfates, alkylbenzene sulfonates, paraffin sulfonates, olefin sulfonates and mixtures thereof.

4. An abrasive-containing liquid detergent composition according to Claim 3 wherein the suds stabilizing nonionic surfactant comprises a material selected from the group consisting of ethanolamides, amine oxides and mixtures thereof.

5. An abrasive-containing liquid detergent composition according to Claim 4 wherein the abrasive comprises a material selected from the group consisting of quartz, silica, diatomaceous earth, feldspar, high density perlite, calcite and mixtures thereof.

6. An abrasive-containing liquid detergent composition according to Claim 5 wherein the particle diameter of said water-insoluble abrasive is from 40 to 125 micrometers.

7. An abrasive-containing liquid detergent composition according to Claim 6 wherein the abrasive comprises a material selected from the group consisting of quartz, silica, feldspar, perlite, calcite and mixtures thereof.

8. An abrasive-containing liquid detergent composition according to Claims 1 or 2 which further comprises a detergency builder selected from the group consisting of alkali metal polyphosphates, water-soluble polycarboxylates, sodium aluminosilicates and mixtures thereof.

9. An abrasive-containing liquid detergent composition according to Claims 1 or 2 wherein the amount of water is from 40% to 75% by weight.

10. An abrasive-containing liquid detergent composition according to Claim 2 wherein the domed portion of the body portion of the closure has an interior horizontal diameter of at least 0.51 cm.

11. An abrasive-containing liquid detergent composition according to Claim 10 wherein the aperture is circular and has a diameter of at least 0.20 cm.

Revendications

1. Composition détergente liquide contenant un abrasif, comprenant en poids:

- (a) de 20 à 35% d'un agent de surface anionique;
- (b) de 2 à 15% d'un agent de surface non-ionique stabilisateur de mousse choisi dans le groupe comprenant les oxydes d'amine, les amides, et les condensats de l'oxyde d'éthylène et d'alcools et d'alkylphénols;
- (c) de 1 à 20% d'un abrasif insoluble dans l'eau ayant une granulométrie de 15 à 150 micromètres et une dureté sur l'échelle de Mohs de 2 à 7; et
- (d) de 20 à 75% d'eau;

cette composition créant une couverture initiale de mousse sur une solution détersive pour la vaisselle et une couverture de mousse après le lavage de huit assiettes quand elle est utilisée à une concentration de 0,07% dans 7,57 litres d'eau à 46°C contenant 120 mg/l d'eau de dureté mesurée en tant que CaCO₃, chaque assiette portant 4,0 ml d'une salissure contenant des triglycérides.

2. Composition détergente liquide contenant un abrasif, dans un récipient distributeur ne se bouchant pas, comprenant:

- (a) une composition détergente liquide contenant un abrasif selon la revendication 1; et
- (b) un récipient imbouchable contenant cette composition détergente liquide, et comprenant:
 - (i) un conteneur plastique souple adapté pour créer une augmentation de la pression interne

par l'application d'une force de compression sur une ou plusieurs zones de sa surface extérieur, et

- (ii) une fermeture distributrice imbouchable, adaptée pour être montée sur le conteneur plastique souple, cette fermeture consistant en une partie corps et en un élément d'obturation du type anse, la partie corps consistant en une jupe annulaire destinée à entourer la bague du conteneur, en un moyen pour fixer cette jupe à la bague du conteneur et en une section verseuse en dôme avec une ouverture centrale, cette ouverture ayant une aire horizontale en section transversale de 1,29 à 16,13 mm², un diamètre minimum de 0,127 cm et une longueur non-supérieure à 0,635 cm, l'élément d'obturation du type anse ayant une conformation incurvée et un joint rotatif le reliant à la partie corps en chaque extrémité, l'élément d'obturation ayant une partie de saisie située centralement et une saillie dépassant vers le bas sur son côté inférieur adaptée pour pénétrer dans la partie extérieure de cette ouverture quand l'élément d'obturation est en position fermée.

3. Détergent liquide contenant un abrasif selon l'une des revendications 1 ou 2, dans lequel l'agent de surface anionique comprend une matière choisie dans le groupe comprenant les alkyl-sulfates, les alkyléthersulfates, les alkylbenzènesulfonates, les paraffinesulfonates, les oléfine-sulfonates et leurs mélanges.

4. Composition détergente liquide contenant un abrasif selon la revendication 3, dans laquelle l'agent de surface non-ionique stabilisateur de mousse comprend une matière choisie dans le groupe consistant en les éthanolamides, les oxydes d'amine et leurs mélanges.

5. Composition détergent liquid contenant un abrasif selon la revendication 4, dans laquelle l'abrasif comprend une matière choisie dans le groupe comprenant le quartz, la silice, le terre de diatomées, le feldspath, la perlite haute densité, la calcite et leurs mélanges.

6. Composition détergent liquid contenant un abrasif selon la revendication 5, dans laquelle la granulométrie de l'abrasif insoluble dans l'eau est comprise entre 40 et 125 micromètres.

7. Composition détergente liquide contenant un abrasif selon la revendication 6, dans laquelle l'abrasif comprend une matière choisie dans le groupe comprenant le quartz, la silice, le feldspath, la perlite, la calcite et leurs mélanges.

8. Composition détergente liquide contenant un abrasif selon l'une quelconque des revendications 1 ou 2, comprenant en outre un adjuvant de détergence choisie dans le groupe comprenant les polyphosphates de métaux alcalins, les polycarboxylates solubles dans l'eau, les aluminosilicates de sodium et leurs mélanges.

9. Composition détergente liquide contenant un abrasif selon l'une quelconque des revendications 1 ou 2, dans laquelle la quantité d'eau est comprise entre 40 et 70% en poids.

10. Composition détergente liquide contenant un abrasif selon la revendication 2, dans laquelle la partie en dôme de la partie corps de la fermeture a un diamètre horizontal intérieur d'au moins 0,51 cm.

11. Composition détergente liquide contenant un abrasif selon la revendication 10, caractérisée en ce que l'ouverture est circulaire et a un diamètre d'au moins 0,20 cm.

Patentansprüche

1. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung, enthaltend, bezogen auf das Gewicht:

(a) 20% bis 35% eines anionischen oberflächenaktiven Mittels;

(b) 2% bis 15% eines schaumstabilisierenden, nichtionischen oberflächenaktiven Mittels ausgewählt aus der Gruppe bestehend aus Aminoxyden, Amiden und den Ethylenoxid-kondensaten von Alkoholen und Alkylphenolen;

(c) 1% bis 20% eines wasserunlöslichen Scheuermittels mit einem Teilchendurchmesser von 15 bis 150 µm und einer Härte auf der Mohs-Skala von 2 bis 7; und

(d) 20% bis 75% Wasser;

wobei diese Zusammensetzung einer Geschirrspüllösung eine anfängliche Schaumdecke und nach dem Waschen von 8 Tellern bei Anwendung in einer Konzentration von 0,07% in 7,57 l Wasser von 46°C, das eine Wasserhärte, gemessen als CaCO₃, von 120 mg/l enthält, wobei jeder Teller 4,0 ml an triglyceridhaltigem Schmutz trägt, eine Schaumdecke liefert.

2. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung in einem Verstopfungen widerstehenden Ausgabebehälter, enthaltend:

(a) eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung gemäß Anspruch 1 und

(b) einen Verstopfungen widerstehenden Behälter, der diese flüssige Reinigungsmittelzusammensetzung enthält, enthaltend;

- (i) einen biegsamen Kunststoffbehälter, der so adaptiert ist, daß er einen Anstieg des Innendruckes durch Anwendung einer Druckkraft auf eine oder mehrere äußere Oberflächenbereiche liefert, und
- (ii) einen Verstopfungen widerstehenden Spenderverschluß, der so adaptiert ist, daß er auf diesem biegsamen Kunststoffbehälter montiert wird, wobei dieser Verschluß aus einem Körperteil und einem bündelartigen Verschlußglied besteht, wobei der Körperteil aus einem ringförmigen Mantel, der das Behälterende umgibt, Einrichtungen zur Befestigung dieses Mantels an diesem Behälterende und einem gewölbten Düsenabschnitt mit einer zentralen Öffnung besteht, wobei diese Öffnung eine waagerechte Querschnittsfläche von 0,0051 cm² bis 0,0635 cm², einen Mindestdurchmesser von 0,127 cm und eine Länge von nicht mehr als 0,635 cm aufweist, wobei dieses bündelartige Verschlußglied eine bogenförmige Gestalt aufweist und an jedem Ende eine drehbare Verbindung zu dem Körperteil hat, wobei dieses Verschlußglied einen zentral angeordneten Griffteil und an seiner Unterseite einen sich nach unten erstreckenden, vorstehenden Teil aufweist, der so adaptiert ist, daß er die Außenseite der Öffnung verschließt, wenn sich das Verschlußglied in geschlossener Stellung befindet.

3. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung gemäß den Ansprüchen 1 oder 2, worin das anionische oberflächenaktive Mittel ein Material ausgewählt aus der Gruppe bestehend aus Alkylsulfaten, Alkylethersulfaten, Alkylbenzolsulfonaten, Paraffinsulfonaten, Olefinsulfonaten und Gemischen daraus umfaßt.

4. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung gemäß Anspruch 3, worin das schaumstabilisierende nichtionische oberflächenaktive Mittel ein Material ausgewählt aus der Gruppe bestehend aus Ethanolamiden, Aminoxiden und Gemischen daraus umfaßt.

5. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung gemäß Anspruch 4, worin das Scheuermittel ein Material ausgewählt aus der Gruppe bestehend aus Quarz, Kieselerde, Diatomeenerde, Feldspat, Perlit hoher Dichte, Calcit und Gemischen daraus umfaßt.

6. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung gemäß Anspruch 5, worin der Teilchendurchmesser des wasserunlöslichen Scheuermittels 40 bis 125 Mikrometer beträgt.

7. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung gemäß Anspruch 6, worin das Scheuermittel ein Material ausgewählt aus der Gruppe bestehend aus Quarz, Kieselerde, Feldspat, Perlit, Calcit und Gemischen daraus, umfaßt.

8. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung gemäß den Ansprüchen 1 oder 2, welche weiterhin einen Detergensgerüststoff ausgewählt aus der Gruppe bestehend aus Alkalimetallpolyphosphaten, wasserlöslichen Polycarboxylate, Natriumaluminosilikate und Gemischen daraus enthält.

9. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung gemäß den Ansprüchen 1 oder 2, worin die Menge an Wasser 40 Gew.-% bis 75 Gew.-% beträgt.

10. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung gemäß Anspruch 2, worin der gewölbte Teil des Körperteils des Verschlusses einen inneren, waagerechten Durchmesser von mindestens 0,51 cm aufweist.

11. Eine Scheuermittel enthaltende flüssige Reinigungsmittelzusammensetzung gemäß Anspruch 10, worin die Öffnung rund ist und einen Durchmesser von mindestens 0,20 cm aufweist.

Fig. 2

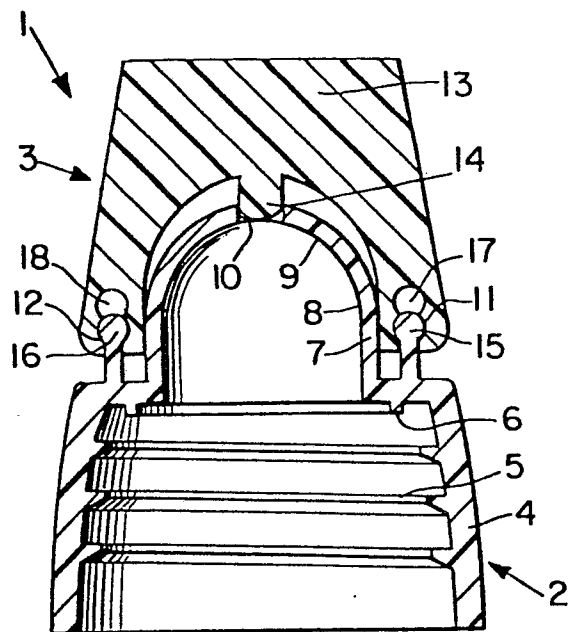


Fig. 1

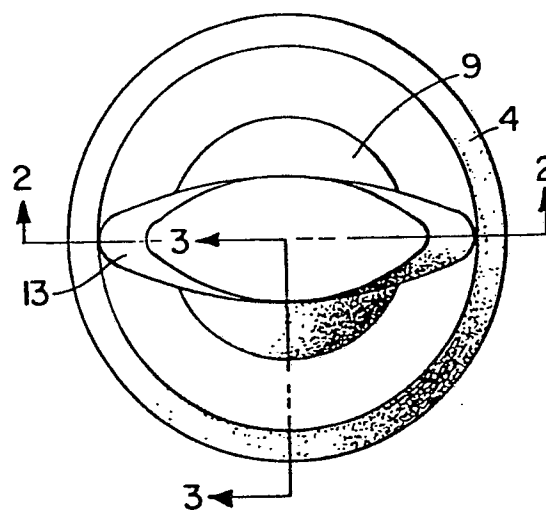


Fig. 3

