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"LIQUID LAUNDRY DETERGENT COMPOSITION  
CONTAINING POLYPHOSPHATE"

The present invention relates to a liquid laundry detergent composition.

Liquid nonaqueous heavy duty laundry detergent compositions are well known in the art. For instance, compositions of that type may comprise a liquid nonionic surfactant in which are dispersed particles of a builder, such as a polyphosphate builder, as shown for instance in U.S. Patents Nos. 4,316,812; 3,630,929; 4,264,466, and British Patents Nos. 1,205,711 and 1,270,040.

It is known that such suspensions can be stabilized against settling by adding an inorganic insoluble thickening agent or dispersant of very high surface area such as finely divided silica of extremely fine particle size (e.g. of 5-100 microns diameter such as sold under the name Aerosil) or the other highly voluminous inorganic carrier materials as disclosed in U.S. Patent 3,630,929, or by including various clays, such as attapulgite, as disclosed in U.S. Patent 4,264,466. Grinding to very fine particle sizes also increases the stability.

We have observed that the stability of the suspension may be increased by including therein an acidic organic phosphorus compound having an acidic - POH group. According to the present invention a liquid nonaqueous or substantially nonaqueous heavy duty laundry detergent composition comprises a suspension of an alkali metal

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- polyphosphate builder salt in a liquid nonionic surfactant, the said composition containing an organic phosphorus compound having an acidic -POH group which compound is present in an amount
5. effective to raise the yield value of the said composition. The organic phosphorus compound may be, for instance, a partial ester of phosphoric acid and an alcohol such as an alkanol which has a lipophilic character, having, for instance, more
  10. than 5 carbon atoms, e.g. 8 to 20 carbon

atoms. It is found that as a result of the inclusion of quite small amounts of the acidic organic phosphorus compound the suspension becomes significantly more stable against settling on standing but remains pourable. Thus, as shown below, inclusion of the acidic phosphorus compound increases the yield value of the suspension, but decreases its plastic viscosity.

It is believed that the use of the acidic phosphorus compound may result in the formation of a high energy physical bond between the -POH portion of the molecule and the surfaces of the inorganic polyphosphate builder so that these surfaces take on an organic character and become more compatible with the nonionic surfactant.

The invention is particularly suitable for use with suspensions in which the particle size of the polyphosphate builder is reduced to below about 10 microns.

The suspensions of the polyphosphate builder, such as sodium tripolyphosphate ("TPP") in the nonionic surfactant are found to behave, rheologically, substantially according to the Casson equation:

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$$\tau^{0.5} = \tau_0^{0.5} + (\eta_{\infty}^{0.5}) \times (\dot{\gamma}^{0.5})$$

$\dot{\gamma}$  is the shear rate,  $\tau$  is the shear stress,  $\tau_0$  is the yield stress (or yield value) and  $\eta_{\infty}$  is the

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- infinite shear rate plastic viscosity (which can be measured by determining the slope of the graph of the square root of the shear stress (as ordinate) vs. the square root of the shear rate). The yield value is the minimum shear stress below which no flow occurs (i.e. it corresponds to the intercept at the ordinate, at zero shear rate, of the graph mentioned above). It is accordingly a criterion of stability. The plastic viscosity is a measure of the flowability once the yield value has been overcome.

- It is preferred that the yield value (measured at 25°C) be at least about 2 Pascals and (for pourability and dispensability) not above about 8 Pascals, such as about 3 to 7 Pascals, more preferably about 4 Pascals.

- For studying this rheological behaviour, one should use a uniform, well defined shear rate viscometer (with either coaxial cylinders or cone-plate geometry) such as a Rheometrics rheometer.

- The suspensions are preferably prepared by grinding a mixture of nonionic surfactant, particles of polyphosphate builder salt and the acidic organic phosphorus compound in a mill which will break down the builder particles to diameters below about 10 microns. The builder salt will generally be supplied as much larger particles of above about 40 microns diameter, such as 100, 200 or 400 microns. If desired, the builder salt may be premixed with the acidic organic phosphorus compound (e.g. by

spraying the acidic compound, dispersed or dissolved in water or volatile organic solvent, onto the builder salt).

- During grinding it is preferred that the proportion of solid ingredients be high enough (e.g. at least about 40% such as about 50%) that the solid particles are in contact with each other and are not substantially shielded from one another by the nonionic surfactant liquid. Mills which employ grinding balls (ball mills) or similar mobile grinding elements have given good results. Thus, one may use a laboratory batch attritor having 8 mm diameter steatite grinding balls. For larger scale work a continuously operating mill in which there are 1 mm or 1.5 mm diameter grinding balls working in a very small gap between a stator and a rotor operating at a relatively high speed (e.g. a CoBall mill) may be employed; when using such a mill it is desirable to pass the blend of nonionic surfactant and solids first through a mill which does not effect such fine grinding (e.g. a colloid mill) to reduce the particle size to less than 100 microns (e.g. to about 40 microns), prior to the step of grinding to an average particle diameter below 10 microns in the continuous ball mill.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

EXAMPLES 1 to 4

Example 1 is a comparison example.

- A nonaqueous heavy duty built liquid detergent composition is prepared by blending nonionic surfactant and sodium tripolyphosphate ("TPP") with other ingredients with and without an acidic organic phosphorus compound, as described below in Table 1, and then grinding the blend in an attritor mill (to reduce the particle size of the suspended ingredients to less than 10 microns). The grinding conditions are identical in each case. grinding for 1/2 hour in an attritor mill containing 8 mm diameter steatite grinding balls, namely in a Wieneroto W-1.S attritor, charged with 2.5 Kg of the mixture.

TABLE 1

| <u>Example</u>               | <u>1</u>     | <u>2</u> | <u>3</u> | <u>4</u> |
|------------------------------|--------------|----------|----------|----------|
| <u>Ingredients</u>           | <u>Parts</u> |          |          |          |
| Proportion of acidic organic |              |          |          |          |
| 20. phosphorus compound (%)  | 0            | 0.1      | 0.2      | 0.3      |
| Yield stress (Pascals)       | 0.3          | 1.6      | 3.2      | 5.6      |
| Plastic viscosity (Pascal    |              |          |          |          |
| seconds)                     | 1.1          | 1.0      | 1.0      | 0.9      |

- The apparent viscosity at any shear rate can be calculated, using the Casson equation and the relationship: apparent viscosity equals shear stress divided by shear rate.

- The acidic organic phosphorus compound in these Examples is a partial ester of phosphoric acid and a C<sub>16</sub> to C<sub>18</sub> alkanol (Empiphos (Registered Trade Mark) 5632 Marchon; it \_\_\_\_\_

is made up of about 35% monoester and 65% diester.

The compositions contain the following ingredients in the proportions specified.

- 35% nonionic surfactant comprising a mixture of
5. equal parts of:
- (a) a relatively water soluble nonionic surfactant which forms a gel when mixed with water at 25°C specifically a C<sub>13</sub> to C<sub>15</sub> alkanol which has been alkoxyated to introduce 10 ethylene oxide and
10. 5 propylene oxide units per alkanol unit and
- (b) a less water-soluble nonionic surfactant specifically a C<sub>13</sub> to C<sub>15</sub> alkanol which has been alkoxyated to introduce 4 ethylene oxide and 7 propylene oxide units per alkanol unit.
15. 12% of the reaction product prepared by mixing 100 g of succinic anhydride with 522 g of the nonionic surfactant known as Dobanol (Registered Trade Mark) 25-7 (the product of ethoxylation of a C<sub>12</sub> to C<sub>15</sub> alkanol, which product has about 7 ethyleneoxide units per
20. molecule of alkanol) and 0.1 g of pyridine (which acts as an esterification catalyst here); heating at 60°C for 2 hours; cooling and filtering to remove unreacted succinic material (infrared analysis indicates that substantially all the free hydroxyls
25. of the surfactant have reacted to form an acidic half ester in which the OH group of the nonionic surfactant has been esterified with one carboxyl group of the succinic anhydride).
- 31.5% TPP in the formulation of Example 1;
30. 31.4% in the formulation of Example 2; 31.3% in the

formulation of Example 3 and 31.2% in the formulation of Example 4.

9% sodium perborate monohydrate,  $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ .

4.5% tetraacetythylenediamine; this is an

5. activator for the sodium perborate,

4% of a copolymer of about equal mole amounts of methacrylic acid and maleic anhydride, completely neutralized to form the sodium salt thereof (Sokalan CP5); this serves to inhibit incrustation (as from

10. formation of dicalcium phosphate).

1% diethylene diamine pentamethylene phosphonic acid sodium salt; this is a sequestering agent having a high stability constant for complexation.

1% proteolytic enzyme slurry (in nonionic  
15. surfactant (Esperase).

1% mix of Na carboxymethylcellulose and hydroxymethylcellulose (an antiredeposition agent) (Relatin DM 4050).

0.5% perfume.

20. 0.5% optical brightener.

The TPP preferably is largely anhydrous material containing a small amount of TPP hexahydrate (e.g. an amount such that the chemically bound water content is about 3%, which corresponds  
25. to about one  $\text{H}_2\text{O}$  per pentasodium tripolyphosphate molecule). Such TPP may be produced by treating anhydrous TPP with a limited amount of water. The presence of the hexahydrate slows down the rapid rate of solution of the TPP in the wash bath and  
30. inhibits caking. One suitable grade of TPP is sold

under the name Thermphos NW; the particle size of this TPP as supplied is in the neighbourhood of 400 microns, its phase I content is about 60%.

- The mixture dispenses readily with cold water
5. in the automatic washing machine. Its specific gravity is about 1.25 and it gives excellent washing when used at a dosage of about 100 grams per wash load (as compared with 170 grams per wash load for the usual heavy duty laundry detergent powders) in
10. conventional European home laundry machines (which employ about 20 litres of water for the washing bath).

- The partial esters of phosphoric acid are known to act as foam suppressants and are mentioned for
15. that purpose in U.S. Patent 4,264,466 (Column 33, lines 34-45). The compositions of this Example are, however, of the low-foaming type; when used to wash conventional wash loads in typical European, e.g. German, front-loading washing machines. They
20. exhibit little foam even in the absence of the partial ester of phosphoric acid and thus do not require any foam suppressant.

- The acidic organic phosphorus compound may be selected from a wide variety of materials, in
25. addition to the partial esters of phosphoric acid and alkanols mentioned above. Thus, one may employ a partial ester of phosphoric or phosphorous acid with a mono or polyhydric alcohol such as hexylene glycol, ethylene glycol, di- or tri-ethylene glycol
30. or higher polyethylene glycol, polypropylene glycol,

- glycerol, sorbitol, or mono- or di-glycerides of fatty acids, in which one, two or more of the alcoholic OH groups of the molecule may be esterified with the phosphorous acid. The alcohol may be
5. a nonionic surfactant such as an ethoxylated or ethoxylated-propoxylated higher alkanol, higher alkyl phenol, or higher alkyl amide. The -POH group need not be bonded to the organic portion of the molecule through an ester linkage; instead it may be
  10. directly bonded to carbon (as in a phosphonic acid, such as a polystyrene in which some of the aromatic rings carry phosphonic acid or phosphinic acid groups; or an alkylphosphonic acid, such as propyl or laurylphosphonic acid) or may be connected to the
  15. carbon through other intervening linkages (such as linkages through O, S or N atoms). Preferably, the carbon:phosphorus atomic ratio in the organic phosphorous compound is at least 3:1, such as 5:1, 10:1, 20:1, 30:1 or 40:1. Among the suitable
  20. compounds are the phosphate ester surfactants described and listed in Kirk-Othmer "Encyclopedia of Chemical Technology", 3rd Edition, Vol. 22 (1983) Pages 359 to 361.

- The particular partial alkyl ester of
25. phosphoric acid and the C<sub>16</sub> to C<sub>18</sub> alkanol, described in the foregoing Examples, is a solid which generally swells, but does not dissolve in the nonionic surfactant. It is supplied as a powder. In a preferred method, used in the Examples, the TPP
  30. is added last (after the other solid ingredients have

been added to the liquid blend of nonionic surfactant and reaction product of succinic anhydride and nonionic surfactant) and the powder of partial alkyl ester of phosphoric acid is added just before the TPP. Acidic organic phosphorus compounds soluble in the nonionic surfactant may also be employed.

As is well known, the nonionic surfactants are characterised by the presence of an organic hydrophobic group and an organic hydrophilic group and are typically produced by the condensation of an organic aliphatic or alkyl aromatic hydrophobic compound with ethylene oxide (hydrophilic in nature). Practically any hydrophobic compound having a carboxy, hydroxy, amido or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a nonionic detergent. The length of the hydrophilic or polyoxyethylene chain can be readily adjusted to achieve the desired balance between the hydrophobic and hydrophilic groups. Typical suitable nonionic surfactants are those disclosed in U.S. Patents 4,316,812 and 3,630,929, as well as those described and listed in the discussion of nonionic surfactants in Kirk-Othmer "Encyclopedia of Chemical Technology", 3rd Edition, Vol. 22 (1983), Pages 360 to 379.

Nonionic surfactants often tend to form gels with limited amounts of cold water; this can sometimes interfere with the complete dispensing of the

- composition from the usual dispenser found in conventional automatic home laundry machines used in Europe. To lower the gelling temperature, and thus promote easier dispensing, there may be included in
5. the composition a carboxylic acid anti-gelling agent. A preferred type of agent of this type is a compound having a carboxylic moiety joined to the residue of a nonionic surfactant, e.g. a half ester of succinic acid or other dicarboxylic acid in which
10. the OH group of the nonionic surfactant has been esterified with one carboxyl group of the acid. This material is preferably in solution in nonionic surfactant.

- The polyphosphate builder salt is preferably an
15. alkali metal (e.g. Na or K) tripolyphosphate, pyrophosphate (e.g. tetrasodium pyrophosphate) or hexametaphosphate. It is preferred that these be largely in anhydrous form. Mixtures of two or more different polyphosphates may be used. The polyphos-
20. phate may also be used in admixture with one or more other water-soluble detergent builders.

- Among other suitable builders are inorganic and organic builder salts such as the phosphates, carbonates, silicates, phosphonates, polyhydroxy-
25. sulphonates, polycarboxylates and the like. Typical suitable builders are those disclosed in U.S. Patents 4,316,812; 4,264,466; and 3,630,929.

- Since, as indicated in the Examples, the compositions of the present invention may be used at
30. relatively low dosages, it is desirable to supplement

any phosphate or phosphate-forming builder (such as sodium tripolyphosphate) with an auxiliary builder such as a polymeric carboxylic acid having high calcium binding capacity, in amount in the range, 5. for instance, of about 1 to 10% of the composition, to inhibit incrustation which could otherwise be caused by formation of an insoluble calcium phosphate. Such auxiliary builders are well known in the art.

10. The composition preferably comprises a peroxygen bleaching agent. This may be a peroxygen compound, such as an alkali metal perborate, percarbonate or perphosphate; a particularly suitable material is sodium perborate monohydrate.

15. The peroxygen compound is preferably used in admixture with an activator therefor. Suitable activators are those disclosed in U.S. Patent 4,264,466 or in column 1 of U.S. Patent 4,430,244. Polyacylated compounds are preferred activators;

20. among these, compounds such as tetraacetyl ethylene diamine ("TAED") and glucose pentaacetate are particularly preferred.

The activator usually interacts with the peroxygen compound to form a peroxyacid bleaching 25. agent in the wash water. It is preferred to include a sequestering agent of high complexing power to inhibit any undesired reaction between such peroxy-acid and hydrogen peroxide in the wash solution in the presence of metal ions. Such a sequestering 30. agent is an organic compound which is able to form

- a complex with  $\text{Cu}^{2+}$  ions, such that the stability constant (pK) of the complexation is equal to or greater than 6, at 25°C, in water of an ionic strength of 0.1 mole/litre, pK being conventionally defined by the formula:  $\text{pK} = -\log K$  where K represent the equilibrium constant. Thus, for example, the pK values for complexation of copper ion with NTA and EDTA at the stated conditions are 12.7 and 18.8, respectively. Suitable sequestering agents include
5. the sodium salts of nitrilotriacetic acid (NTA);
  10. ethylene diamine tetraacetic acid (EDTA); diethylene triamine pentaacetic acid (DETPA); diethylene triamine pentamethylene phosphonic acid (DTPMP); and ethylene diamine tetramethylene phosphonic acid (EDITEMPA).
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- Other ingredients which may be included in the composition include enzymes (e.g. proteases, amylases or lipases or mixtures thereof), optical brighteners, antiredeposition agents, and colourants
20. (e.g. pigments or dyes).

- The composition may also contain an inorganic insoluble thickening agent or dispersant of very high surface area such as finely divided silica of extremely fine particle size (e.g. of 5-100 milli-
25. microns diameter such as sold under the name (Aerosil (Registered Trade Mark)) or the other highly voluminous inorganic carrier materials disclosed in U.S. Patent 3,630,929, in proportions of 0.1-10%, e.g. 1 to 5%.
  30. For best results it is preferable, however, that compositions containing peroxygen compound and

activator therefor) be substantially free of such compounds and of other silicates; it has been found, for instance, that silica and silicates promote the undesired decomposition of the peroxyacid. In addition, the use of these water-insoluble inorganic materials can present other problems in the system. No voluminous silica or chain structure type clay is needed in the practice of the present invention and the composition is preferably substantially free of such materials.

While in the preferred compositions the average particle size of the solids has been reduced to less than about 10 microns (e.g. typically only about 5-10% of the solids content has a particle size above 10 microns), the invention may also be applied to compositions which have not been so finely ground. It will be understood that finer grinding increases the stability of the composition against settling on standing; according to Stokes law the smaller the particle size the lower the rate of sedimentation. By raising the yield value obtained with a given degree of grinding, the use of the acidic phosphorus compound can make it possible to increase the stability of compositions in which the average particle diameter is say 15, 20, or 25 microns, as by using increased amounts of the acidic phosphorus compound to attain the desired yield value of at least about 2 Pascals.

In the compositions of the invention, typical proportions of the ingredients are as follows:

Suspended detergent builder, within the range of about 10 to 60%, such as 20 to 50%, e.g. about 25 to 40%;

- Liquid phase comprising nonionic surfactant
5. (and, optionally, dissolved carboxylic acid gel-inhibitor) within the range of about 30 to 70%, such as about 40 to 60%; this phase may also include a diluent such as a glycol, e.g. polyethylene glycol (e.g. "PEG (Registered Trade Mark) 400") or hexylene glycol.
10. Carboxylic acid antigelling agent, in an amount to supply in the range of about 0.5 to 10 parts (e.g. about 1 to 6 parts, such as about 2 to 5 parts) of -COOH (M.W.45) per 100 parts of the blend of such compound and the nonionic surfactant;
15. typically the amount of this anti-gelling agent is in the range of about 0.01 to 1 part per part of nonionic surfactant, such as about 0.05 to 0.6 part, e.g. about 0.2 to 0.5 part;
- Peroxygen compound (such as sodium perborate
20. monohydrate) in the range of about 2 to 15%, such as about 4 to 10%;
- Activator, in the range of about 1 to 8%, such as about 3 to 6%;
- Sequestering agent of high complexing power, in
25. the range of about 0.25 to 3%, such as about 0.5 to 2%;
- Acidic organic -POH compound, in the range of 0.01 to 5%, such as about 0.05 to 2%, e.g. about 0.1 to 1%.
30. In this application all proportions are by

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weight unless otherwise indicated. In the Examples  
atmospheric pressure is used unless otherwise  
indicated.

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CLAIMS

1. A liquid nonaqueous or substantially nonaqueous heavy duty laundry detergent composition comprising a suspension of an alkali metal polyphosphate builder salt in a liquid nonionic surfactant, the said composition containing an organic phosphorus compound having an acidic -POH group which compound is present in an amount effective to raise the yield value of the said composition.
5. 10. 2. A composition as claimed in Claim 1 in which the said composition is substantially non-aqueous and has a yield value in the range of about 2 to 8.
15. 3. A composition as claimed in Claim 1 or Claim 2 in which the said composition is of the low-foaming type even in the absence of the said organic phosphorus compound.
20. 4. A composition as claimed in any one of Claims 1 to 3 in which the said polyphosphate salt is sodium tripolyphosphate.
25. 5. A composition as claimed in any one of Claims 1 to 4 in which the particle size of the said suspended builder salt is less than about 10 microns.
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6. A composition as claimed in any one of Claims 1 to 5 in which the carbon to phosphorus atomic ratio in the said phosphorus compound is at least about 3:1.
- 5.
7. A composition as claimed in any one of Claims 1 to 6 in which the said organic phosphorus compound is a partial ester of an alkanol and phosphoric acid.
- 10.
8. A composition as claimed in Claim 7 in which the said alkanol is a higher alkanol.
9. A composition as claimed in any one of
15. Claims 1 to 8 which has been prepared by grinding the said suspension until the particle size of the said suspended builder salt is less than about 10 microns.
20. 10. A composition as claimed in any one of Claims 1 to 9 in which the said composition is substantially nonaqueous and contains a peroxygen bleach.
25. 11. A composition as claimed in Claim 10 in which the said peroxygen bleach comprises sodium perborate and an activator therefor.
12. A composition as claimed in Claim 11 in
30. which the said activator is tetraacetylene-diamine.



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13. A composition as claimed in any one of Claims 1 to 12 substantially free of silica or silicate thickening agent.

5. 14. A composition as claimed in any one of Claims 1 to 13 substantially free of chain structure type clay.

10. 15. A composition as claimed in any one of Claims 1 to 14 which contains a carboxylic acid anti-gelling agent.

15. 16. A composition as claimed in Claim 1 substantially as specifically described herein with reference to Example 2, 3 or 4.

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