

United States Patent [19]

[11] **3,720,621**

Smeets

[45] **March 13, 1973**

[54] **AQUEOUS DETERGENT COMPOSITIONS**

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[22] Filed: **June 15, 1970**

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[21] Appl. No.: **46,472**

[57] **ABSTRACT**

[30] **Foreign Application Priority Data**

June 17, 1969 Great Britain.....30,640/69

The present invention provides a homogeneous liquid composition containing by weight:

[52] U.S. Cl.**252/135, 252/99, 252/112, 252/525, 252/526, 252/540, 252/544, 252/545, 252/559**

a. from 14 to 35 percent of sodium tripolyphosphate,

[51] Int. Cl.**C11d 3/04, C11d 7/00**

b. from 0.1 to 50 percent at least of a potassium and/or ammonium salt of an inorganic or organic acid,

[58] Field of Search.....**252/99, 135, 137, 138, 152, 252/161; 8/111**

c. from 15 to 85.9 percent of water.

The composition is especially useful as a detergent for non-porous surfaces and textile materials.

[56] **References Cited**

12 Claims, No Drawings

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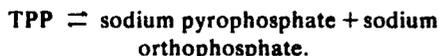
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AQUEOUS DETERGENT COMPOSITIONS

The present invention relates to aqueous detergent compositions which, although containing proportions of sodium tripolyphosphate greater than the saturation concentration of the said salt in water, are nevertheless in the form of substantially homogeneous solutions. Such compositions may be used particularly for the cleansing of articles having non-porous surface and for the washing of textile materials.

Sodium tripolyphosphate (hereinafter referred to as TPP) is the alkali metal phosphate conventionally used in solid detergent compositions for domestic and/or industrial use, for several reasons: it is a sequestering agent for heavy cations in water and provides water-softening properties, it reinforces the detergent action of anionic and/or non-ionic surface-active agents currently used in detergent compositions, it contributes to a marked degree the removal of soil on articles during cleansing and ensures the formation of stable suspensions of the detached soil particles in the wash liquid, and it has little corrosive action on metals and/or metal alloys used in the construction of washing machines, wash-vessels and the like. To such diverse advantages of TPP there is added a low manufacturing cost, which provides an explanation why it is in practice pre-eminent over other alkali-metal polyphosphates, for example sodium pyrophosphate or sodium hexametaphosphate.

TPP has a relatively low solubility in water, the saturation concentration in water at room temperature being about 164 g/liter, corresponding to about 14 percent by weight. Such low solubility is not a disadvantage for solid detergent compositions, which may for example be in the form of powder, granules, flakes or the like. However such low solubility represents a practically insolvable problem in the formulation of homogeneous liquid detergent compositions, due to the fact that these normally require a TPP content of about 18 to 40 percent by weight as this is the level of concentration in most commercial solid detergent compositions. In fact the proportion of TPP capable of being introduced into liquid detergent compositions is substantially lower than the theoretical 14 percent by weight (which is the saturation concentration of TPP) due to the presence particularly of surface-active agents. A well-known effect is that surface-active agents and TPP have a mutual effect on their respective solubilities, the higher the concentration of surface-active agent in liquid compositions the less the solubility of TPP, and vice versa. Another problem, also affecting the solubility of TPP is its resistance to hydrolysis. It is known that in the presence of water, the hydrolysis tends to form an equilibrium according to the equation



Such a condition detracts from the useful properties of TPP.

There is at the present time an increasing tendency to use liquid detergent compositions instead of solid detergent compositions. The superiority of such liquid compositions includes the following:

a. they are homogeneous, solid compositions presenting difficulty due to differences in granulation and the specific gravity of the constituent ingredients;

b. liquid compositions are more easily delivered in measured doses than solid compositions in automatic washing machines (no blockage or residue or formation of dust);

c. they may be applied locally to the article being cleaned, etc.

Current liquid detergent compositions contain in practice phosphates (pyrophosphate, tripolyphosphate) only in the form of their potassium salts, as they are more soluble than the corresponding sodium salts (cf. O. PFRENGLE and C. PIETRUCK, *Fette.Seifen.Anstrichmittel*, 64, (1962), pages 321-326). By this means, it is possible to provide concentrations of phosphates which are approximately of the same order of magnitude as the conventional solid compositions. But potassium pyrophosphate and tripolyphosphate are more sensitive than their sodium equivalents. There is interest therefore in providing liquid detergent compositions in which the phosphate content is predominantly sodium tripolyphosphate, and it is to solving this problem that the present invention is directed.

The applicants have discovered that it is possible to prepare liquid aqueous detergent compositions containing proportions of sodium tripolyphosphate considerably higher than the limit of solubility thereof in water, under normal conditions, in other words in a concentration greater than 14 percent by weight and up to 35 percent by weight, by the presence in the compositions with sodium tripolyphosphate of a suitable proportion of an inorganic or organic potassium and/or ammonium salt together subsequently with desired surface-active agents, solubilizing agents, organic sequestering agents, and other adjuvants conventionally used in solid and/or liquid detergent compositions, per-compounds, the rest being water.

The object of the present invention provides homogeneous liquid detergent compositions comprising the following composition:

a. from 14 to 35 percent by weight of sodium tripolyphosphate,

b. from 0.1 to 50 percent by weight at least of a potassium and/or ammonium salt of an inorganic or organic acid;

c. from 0 to 35 percent by weight at least of a salt of a sulphonated ester of a polycarboxylic acid,

d. from 0 to 20 percent by weight at least of an anionic surface-active agent,

e. from 0 to 15 percent by weight at least of a non-ionic surface-active agent,

f. from 0 to 20 percent by weight at least of a solubilizing agent,

g. from 0 to 20 percent by weight at least of an organic sequestering agent,

h. from 0 to 20 percent by weight at least of a per-compound,

i. from 0 to 5 percent by weight in total of coloring agents, scents, bodying agents, optical whiteners, anti-corrosion agents and anti-staining agents,

j. water to make up to 100 percent.

a. The sodium tripolyphosphate, $\text{Na}_3\text{P}_3\text{O}_{10}$, used in the aqueous detergent compositions according to the invention, may be used in any of its crystallographic forms and in any state of hydration, from the anhydrous form $\text{Na}_3\text{P}_3\text{O}_{10}$ to the hexahydrate compound $\text{Na}_3\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$

10-6H₂O. It is present in the compositions according to the invention in a concentration of from 14 to 35 percent by weight, preferably from about 18 percent to about 28 percent by weight, depending on the intended use of the composition and depending on the concentration of other ingredients present therein.

b. The potassium and/or ammonium salt used to enhance the solubility of the TPP in the aqueous detergent compositions according to the invention may be a salt of an inorganic acid for example a sulphate, chloride, nitrate, carbonate, bicarbonate, borate, orthophosphate, metaphosphate, pyrophosphate and the like, or may be a salt of an organic acid, for example a maleate, adipate, aconitate, citrate, tartrate, ethylenediamine-tetracetate, nitrilotriacetate, diethylene-triamine-pentacetate, succinate or the like. Although inorganic and organic sodium salts diminish the solubility of TPP in water, inorganic or organic potassium and/or ammonium salts used according to the invention enhance the solubility as hereinafter described. However the nature of the inorganic or organic anion of the potassium and/or ammonium salt incorporated in the compositions influences the solubility of TPP to a considerable extent. Thus by way of example, potassium sulphate is more effective than potassium chloride, and the carbonate more effective than the bicarbonate. As a result, the potassium and/or ammonium salt may be present in a proportion of down to 0.1 percent by weight or up to 50 percent by weight, based on the total aqueous detergent composition. For obvious economic reasons, no more of the potassium salt should be used than is necessary, a portion of from 1 to 10 percent by weight based on the total composition, is preferred.

Potassium pyrophosphate is the preferred potassium salt. It is effective not only as a sequestering agent which enhances the solubility of TPP in water, but the applicants have discovered that it effectively stabilizes the tripolyphosphate agent hydrolysis in aqueous solution into sodium pyrophosphate and sodium orthophosphate (as shown in the experiments hereinafter described). It is therefore particularly interesting to introduce potassium pyrophosphate in the aqueous detergent compositions of the present invention. The content should not therefore be too great so as to undergo a double-decomposition reaction with TPP to form sodium pyrophosphate, which as is well known, has a very low solubility in water and therefore tends to separate out as a precipitate. The applicants investigations have shown that the optimum proportion of potassium pyrophosphate incorporated in the liquid detergent compositions according to the invention is between 5 and 25 percent based on the TPP present in the said compositions.

c. The salts of sulphonated esters of a polycarboxylic acid which may be used as surface-active agent according to the present invention have properties superior to anionic and non-ionic surface-active agents for the production of liquid detergent compositions due to the fact that (1) they are equally effective at lesser concentrations, (2) they are more soluble in water, (3) they have a greater resistance to salting out by electrolytes and (4) they have solubilizing properties as shown in the Examples hereinafter described.

Examples of such salts of sulphonated esters of polycarboxylic acids are the potassium salts of sulphonated derivatives of one or more alpha-beta unsaturated di- or tri-carboxylic acids esterified with the hydroxyl group of one or more non-ionic surface-active agents described in the Applicants British Pat. Specification No. 47677/67, or the potassium salts of sulphonated polycarboxylic acids partially esterified by the hydroxyl group of one or more non-ionic surface-active agents, as described in the Applicants British Pat. Specification No. 31014/67, or the potassium salts of sulphonated polycarboxylic acids esterified with the hydroxyl group of a non-ionic surface-active agent, as described in the Applicants British Pat. Specification No. 59220/68. Instead of such potassium salts, it is possible to use sodium salts or organic amine salts, for example triethanolamine salts.

The following specific examples of such compounds are provided: For the compounds 1 to 6 inclusive, the starting acid is an unsaturated polycarboxylic acid obtained by the pyrolysis of calcium citrate according to the procedure described in the Applicants British Pat. Specification No. 31014/67.

Compound No. 1 (termed ASP 1) is obtained by reacting the pyrolysis product of calcium citrate with a sulphur-containing anhydride to fix an SO₃H group across the double bond to obtain after acidification a sulphonated polycarboxylic acid. A quarter of the COOH groups of the said acid is esterified with a non-ionic surface-active agent obtained by ethoxylating a C₁₂-C₁₄ linear alcohol with 6 moles of ethylene oxide (E.O.). The remaining three-fourths of the COOH groups and the SO₃H group are then neutralized with potassium hydroxide (see British Pat. Specification Nos. 59220/68 and 31014/67).

Compound No. 2 (ASP 2) is the same as ASP 1, except that the non-ionic agent is a C₁₂-C₁₄ alcohol ethoxylated with 3 moles of E.O.

Compound No. 3 (ASP 3) is the same as ASP 1, except that the non-ionic agent is nonylphenol ethoxylated with 6 moles of E.O.

Compound No. 4 (ASP 4) is the same as ASP 1, except that the non-ionic agent is a secondary C₁₁-C₁₅ /ethoxylated with 7 moles of E.O.

Compound No. 5 (ASP 5) is similar to ASP 4, but it was neutralized with sodium hydroxide.

Compound No. 6 (ASP 6) is similar to ASP 1, but the non-ionic agent is a C₁₆-C₁₈ alcohol ethoxylated with 9 moles of E.O.

Compound No. 7 (ASP 7) is the sulphonated product of aconitic acid, in other words sulphotricarballic acid, a carboxyl group of which is esterified with a non-ionic agent obtained by ethoxylating nonylphenol with 8.5 moles of E.O. and then neutralizing two of the remaining COOH groups and the SO₃H group with potassium hydroxide (see British Pat. Specification No. 47677/67).

Compound No. 8 (ASP 8) is the sulphonated product of maleic acid, that is to say sulphosuccinic acid, a carboxyl group of which was esterified with a non-ionic agent obtained by ethoxylating a C₁₂-C₁₄ linear alcohol with 6 moles of E.O. and neutralizing the remaining carboxyl group and the SO₃H group with potassium hydroxide (see British Pat. Specification 47677/67).

The sulphopolycarboxylic acids, represented by compounds 1 to 8 hereinbefore described, are able to be used in the liquid detergent compositions according to the invention in a proportion of from 0 to 35 percent by weight based on the total composition, preferably from 1 to 20 percent by weight.

d. Anionic surface-active agents for use in the liquid detergent compositions according to the invention are particularly selected from the group of soaps, sulphonates and organic synthetic sulphates. The soaps are preferably C₁₀-C₂₂ fatty acid soaps, for example coconut fatty acids or tallow fatty acids. The sulphonates and organic synthetic sulphates are preferably selected from the following groups:

1. Sulphonates of olefines containing eight to 25 carbon atoms, for example sodium or potassium dodecyl sulphonate,
2. Alkylbenzene sulphonates the alkyl groups of which contain from 10 to 16 carbon atoms and which may be straight-chain or branched, for example potassium salts of decyl-, undecyl-, dodecyl-, tridecyl-, tetradecyl-, pentadecyl- or hexadecyl sulphonic acids,
3. Secondary alkyl sulphates, of the type obtainable under the Trade Mark "TEEPOL,"
4. Primary aliphatic alcohol sulphates containing from eight to 18 carbon atoms, for example lauryl- or hexadecyl potassium sulphates,
5. Alkyl- or alkylaryl-polyoxyethylene potassium sulphates of which the alkyl group contains from eight to 18 carbon atoms, and the alkylaryl group contains a C₈-C₁₈ alkyl group and an aryl group, preferably phenyl, and the polyoxyethylene group preferably contains from 1 to 4 moles of E.P.

The anionic surface-active agent of the types hereinbefore described is used in the liquid detergent compositions according to the invention in proportions of from 0 to 20 percent by weight based on the total composition, preferably from 1 to 15 percent by weight.

e. The non-ionic surface-active agent which may be used in the liquid detergent compositions of the present invention is preferably selected from the following groups:

1. ethoxylated alkylphenols containing from six to 12 carbon atoms in the alkyl chain and from 3 to 25 moles of E.O. per mole of alkyl phenol,
2. Primary or secondary ethoxylated C₈-C₂₂ alcohols derived from natural or synthetic alcohols and containing from 1 to 50 moles of E.O. per molecule of alcohol,
3. Alkanolamides and ethoxylated alkylamides, for example the diethanolamide of ethoxylated coconut fatty acids,
4. Copolymers derived from different alkylene oxides, known commercially under the Trade Mark "PLURONIC," and polymers such as polyethylene glycol and propylene glycol,
5. Esters of polyhydroxy compounds, for example sucrose stearate, lauryl sucrose and the like,
6. Tertiary amine oxides and tertiary phosphine oxides, for example dimethyldodecylamine oxide, N-dodecylmorpholine oxide, dodecyldimethylphosphine oxide and the like.

The non-ionic surface-active agent hereinbefore described is incorporated in compositions according to

the invention in proportions of from 0 to 15 percent by weight based on the total composition, preferably from 1 to 10 percent by weight.

As will be shown in Example 2, the anionic surface-active agents quoted as (d), as do the non-ionic surface-active agents quoted as (e), provide a substantially lower resistance to salting out the surface-active agents of the sulpho-polycarboxylic acid ester type quoted under (c). This is because they are used in the minimum quantities to provide the detergent properties required without salting out in the aqueous liquid detergent compositions of the invention. If it is desired to use considerably greater proportions, in other words close to the upper limit of the concentration hereinbefore specified, it is then necessary to employ a solubilizing agent or a mixture of a solubilizing agent with a sulphopolycarboxylic acid of the type quoted under (c).

f. The solubilizing agent is an organic compound which enhances the water-solubility of a sparingly-soluble substance. Known examples of such agents are xylene sulphonic acids, p-toluene sulphonic acids, p-cumene sulphonic acids and the like, preferably used in the form of their potassium salts. However, as is shown particularly in Example 3, the solubilizing agent may be replaced partially by a potassium salt of an ester of a sulpho-carboxylic acid described under (c). Such partial replacement is advantageous because the ester of the sulpho-polycarboxylic acid has excellent detergent properties, such properties being absent from the solubilizing agent therein which therefore constitutes an inactive component in the aqueous liquid detergent compositions of the invention.

The solubilizing agent is used in proportions of from 0 to 20 percent by weight of the total aqueous liquid detergent composition, preferably in proportions of from 1 to 12 percent by weight.

g. The organic sequestering agent used according to the invention is an aminopolycarboxylic acid such as ethylene-diamine-tetracetic acid (EDTA), nitrilotriacetic acid (NTA), diethylene-triamine-pentacetic acid (DTPA) or a hydroxylpolycarboxylic acid, or the like, preferably used in the form of the potassium salt. The sequestering agent may be in the form of water-soluble complexes with heavy ions responsible for water hardness (calcium, magnesium and the like). The compositions of the invention may contain from 0 to 20 percent by weight based on the total composition, preferably from 0.5 to 10 percent by weight.

h. The per-compound subsequently incorporated in the compositions of the invention is a water-soluble per-compound, for example hydrogen peroxide, perborate, percarbonate or a persulphate, preferably the potassium compound thereof. The quantity of per-compound added is from 0 to 20 percent by weight based on the total aqueous liquid detergent composition, preferably from 1 to 5 percent by weight.

i. Compositions according to the invention may contain adjuvants conventionally used in liquid and/or solid detergent compositions. Such adjuvants are for example coloring agents, scents, thickening agents such as carboxymethyl cellulose, polyvinylpyrrolidone, polyvinyl alcohol or the like, optical whiteners, anti-corrosion agents, anti-staining agents or the like. The total proportion of such adjuvants is from 0 to 5 per-

cent by weight based on the total liquid detergent composition, preferably from 1 to 4 percent by weight.

j. The compositions of the invention contain water in at least the proportion necessary to obtain a liquid detergent composition.

From the foregoing it is apparent that a wide variety of liquid detergent compositions according to the invention may be obtained containing many different constituents as hereinbefore described. The common factor is that they must contain a proportion of TPP more than 164 g/liter (i.e., 14 percent by weight), which to the knowledge of the applicants has not previously been in liquid detergent compositions, and that they must contain a potassium or ammonium salt of an inorganic or organic acid in a proportion sufficient to ensure the solubility in water of the TPP. The other constituents of the compositions of the invention are optional and are selected in a proportion according to the end use of the compositions.

To prepare the compositions according to the invention, a method may be used as hereinafter described which is given by way of example only and which is not intended to be limiting:

About 50 to 60 percent of the final water is introduced into a vessel, and there is added thereto with agitation the surface-active agents of type (c), (d) and/or (e), coloring agent, scent, thickening agent, anti-corrosion agent and anti-staining agent. The solubilizing agent and then the optical whitener is added, and agitation is continued until a homogeneous solution is obtained. Subsequently, while agitation is continued, the potassium salts and then water up to about 85 percent of the final quantity is added, and the TPP is then added with vigorous agitation, and when it is dissolved the solution is filtered. The per-compound is then added, and to adjust the pH to between about 7 and 9, either sulphuric acid or potassium hydroxide is added, and the water made up to the full quantity.

Amongst the particular uses to which the liquid compositions of the invention may be put, there may be mentioned water-softening, the cleansing of articles having a non-porous surface, for example glass, porcelain, enamel, wood, metal, layers coated with plastics materials for example in vehicle building, and the like, and similarly the washing of textile materials of all kinds, i.e. natural or synthetic textiles, whether for light duty washing or heavy duty washing.

The following non-limiting Examples are provided to illustrate liquid detergent compositions according to the invention.

EXAMPLE 1

Effect of Potassium Salts on the solubility in water of TPP

Solutions were prepared containing increasing quantities of solubilizing salt (potassium or ammonium salt). To 100 mls. of each of the solutions were added, with vigorous agitation, sodium tripolyphosphate in a quantity such that a proportion thereof remained undissolved. The suspension thus obtained was agitated during a period of 1 hour with a magnetic agitator, and then left overnight at room temperature.

The suspension was then filtered and the proportion of sodium tripolyphosphate in solution determined using the following analytical techniques:

- determination of sodium in solution by flame photometry,
- colorimetric determination of the phosphate ion in the form of ammonium molybdate and ammonium monovanadate, using a spectrophotometer.

Other substances were measured by classical chemical analytical procedures.

The sodium tripolyphosphate was used in the form of the hexahydrate, because the anhydrous form produces a supersaturated solution which subsequently crystallizes out. In all the following Examples, the contents are expressed in grams per liter. The TPP is expressed as g/liters as the anhydride equivalent.

| | | | | | | |
|----|--|--|---|--|---|--|
| 15 | Effect of NaCl and KCl | | | | | |
| | NaCl | Na ₃ P ₃ O ₁₀ | KCl | Na ₃ P ₃ O ₁₀ | | |
| | 0 | 163 | 0 | 163 | | |
| | 50 | 86 | 35 | 194 | | |
| | 101 | 46 | 74 | 202 | | |
| | 201 | 34 | 195 | 185 | | |
| 20 | Effect of Na ₂ SO ₄ , K ₂ SO ₄ and (NH ₄) ₂ SO ₄ | | | | | |
| | Na ₂ SO ₄ | Na ₃ P ₃ O ₁₀ | K ₂ SO ₄ | Na ₃ P ₃ O ₁₀ | (NH ₄) ₂ SO ₄ | Na ₃ P ₃ O ₁₀ |
| | 0 | 163 | 0 | 163 | 0 | 163 |
| | 42 | 152 | 8.7 | 174 | 19 | 205 |
| | 82 | 138 | 17 | 193 | 41 | 238 |
| | 145 | 112 | 33 | 205 | 74 | 271 |
| | | | 51 | 227 | 213 | 289 |
| | | | 68 | 247 | 340 | 219 |
| | | | 88 | 252 | | |
| 30 | Effect of Na ₂ CO ₃ , KHCO ₃ and K ₂ CO ₃ | | | | | |
| | Na ₂ CO ₃ | Na ₃ P ₃ O ₁₀ | KHCO ₃ | Na ₃ P ₃ O ₁₀ | K ₂ CO ₃ | Na ₃ P ₃ O ₁₀ |
| | 0 | 164 | 0 | 164 | 0 | 164 |
| | 54 | 111 | 45 | 212 | 44 | 230 |
| | 105 | 80 | 92 | 235 | 222 | 301 |
| | 264 | 41 | 230 | 270 | 435 | 288 |
| 35 | Effect of KBO ₂ and KBO ₂ ·H ₂ O ₂ | | | | | |
| | KBO ₂ | Na ₃ P ₃ O ₁₀ | KBO ₂ ·H ₂ O ₂ | Na ₃ P ₃ O ₁₀ | | |
| | 0 | 164 | 0 | 164 | | |
| | 15 | 198 | 22 | 230 | | |
| | 39 | 223 | 52 | 285 | | |
| | 76 | 259 | 100 | 336 | | |
| | 191 | 291 | | | | |
| 40 | Effect of sodium citrate·2H ₂ O and potassium citrate·H ₂ O | | | | | |
| | Na ₃ citrate | Na ₃ P ₃ O ₁₀ | K ₂ citrate | Na ₃ P ₃ O ₁₀ | | |
| | 0 | 164 | 0 | 164 | | |
| | 65 | 130 | 17 | 185 | | |
| | 114 | 102 | 45 | 220 | | |
| | 262 | 54 | 87 | 240 | | |
| | 543 | 22 | 218 | 264 | | |
| 45 | Effect of potassium aconitate and potassium maleate | | | | | |
| | K ₂ aconitate | Na ₃ P ₃ O ₁₀ | K ₂ maleate | Na ₃ P ₃ O ₁₀ | | |
| | 0 | 164 | 0 | 164 | | |
| | 40 | 207 | 39 | 193 | | |
| | 83 | 224 | 79 | 215 | | |
| | 207 | 245 | 201 | 221 | | |
| | 412 | 231 | | | | |
| 50 | Effect of K salts of E.D.T.A. ⁽⁺⁾ and N.T.A. ⁽⁺⁺⁾ | | | | | |
| | K ₄ E.D.T.A. | Na ₃ P ₃ O ₁₀ | K ₂ N.T.A. | Na ₃ P ₃ O ₁₀ | | |
| | 0 | 164 | 0 | 164 | | |
| | 25 | 176 | 25 | 174 | | |
| | 70 | 182 | 70 | 185 | | |
| | 140 | 188 | 140 | 187 | | |
| | 270 | 179 | | | | |

(+) E.D.T.A. : ethylene-diamine-tetracetic acid.

(++) N.T.A. : nitrolo-triacetic acid.

The preceding tables show that invariably sodium salts lower the solubility of the sodium tripolyphosphate and that potassium and ammonium salts increase the solubility thereof. It is equally to be seen that certain salts used according to the invention are substantially better than potassium tripolyphosphate in their solubilizing effect on TPP.

EXAMPLE 2

Resistance to salting out of surface-active agents by electrolytes

The method of determining the resistance to salting out is as follows:

For each surface-active material used, three aqueous solutions were prepared containing respectively 1 percent, 5 percent and 10 percent by weight of active material. A solution was prepared containing 900 g/liter of potassium citrate monohydrate and used for titrating the three solutions of active material. The quantity of citrate was noted which was required to be added to each of these solutions to produce phase separation. On a graph of the three quantities of citrate corresponding to three concentrations of surface-active material; there is obtained a straight line which on extrapolation determines the notional concentration of citrate corresponding to 0 percent of surface-active material, in order to be able to compare their resistance to salting out of the several active materials by electrolytes.

| Surface-active material | Resistance to salting out: concentration in g/l of potassium citrate anhydride extrapolated to 0% of active material |
|---|--|
| ASP 1 | 555 |
| ASP 2 } potassium salts | 620 |
| ASP 3 } of esters of sulpho- | 330 |
| ASP 4 } polycarboxylic acids | 482 |
| ASP 5 } (ASP 5 = sodium salt) | 425 |
| ASP 7 | 292 |
| ASP 8 | 316 |
| Potassium-linear alkyl-benzene-sulphonate | very slightly soluble |
| lauryl-ether-sulphate with 3.5 moles of E.O. | 180 |
| C ₁₂ -C ₁₄ alcohol ethoxylated with 6 moles of E.O. | 70 |
| nonyl phenol ethoxylated with 8.5 moles of E.O. | 25 |
| C ₁₁ -C ₁₅ secondary alcohol with 7 moles of E.O. | 50 |

The table shows that the salts of esters of sulphopolycarboxylic acids of group (c), preferably used as surface-active agents, have a resistance to salting out by electrolytes clearly superior to anionic and non-ionic surface-active agents of groups (d) and (e).

These results are confirmed by the following data of the determination of the maximum quantity (in g/liter) of the surface-active agents that it is possible to introduce in an aqueous detergent solution containing 200 g/liter of TPP, 20 g/liter of potassium pyrophosphate and 20 g/liter of potassium sulphate, without phase-separation (see the Tables hereinafter set forth):

| | |
|--|---------|
| ASP 2 } potassium salts of esters of | 220 g/l |
| ASP 3 } sulphopolycarboxylic acids | 200 g/l |
| ASP 5 } (ASP 5 = sodium salt) | 220 g/l |
| potassium linear alkyl(C ₁₂ -C ₁₄)-benzene-sulphonate | <30 g/l |
| potassium lauryl-ether-sulphate with 3.5 moles of E.O. | <80 g/l |
| potassium alkyl(C ₁₂ -C ₁₄)-sulphate | <20 g/l |
| C ₁₂ -C ₁₄ alcohol ethoxylated with 6 moles of E.O. | <20 g/l |
| nonylphenol ethoxylated with 8.5 moles of E.O. | <20 g/l |

EXAMPLE 3

The solubilization of salts of esters of sulphopolycarboxylic acids

It is to be seen from Example 2 that current anionic and non-ionic surface-active agents have a tendency to be salted out by electrolytes at relatively low concentrations of surface-active agents. To militate against this tendency there may be added to the detergent compositions a solubilizing agent (hydrotropic agent).

In the present Example there is used a liquid detergent composition which contains a potassium salt of an ester of a sulphopolycarboxylic acid (ASP 1), the commercially-available non-ionic surface-active agent TERGITOL 15S3 which is the condensation product of a C₁₁-C₁₅ secondary alcohol with 3 moles of E.O., TPP, potassium pyrophosphate and potassium xylene-sulphate (P.X.S.), the latter being the solubilizing agent.

It is to be seen from Table I that for preventing the detergent composition from separating out into two phases, it is necessary to increase the concentration of P.X.S. as the concentration of TERGITOL 15S3 is increased.

It is to be seen from Table II that the content of P.X.S. may be diminished as the content of ASP 1 is increased, thus demonstrating the solubilizing effect of this compound.

In the said two Tables, the numerical values are expressed as g/liter.

TABLE I

| Test No. | ASP 1 | Tergitol 15S3 | TPP | K.pyro-phosphate | P.X.S. |
|----------|-------|---------------|-----|------------------|--------|
| 35 1 | 80 | 0 | 180 | 20 | 0 |
| 2 | 80 | 10 | 180 | 20 | 5 |
| 3 | 80 | 20 | 180 | 20 | 20 |
| 4 | 80 | 30 | 180 | 20 | 50 |
| 5 | 80 | 40 | 180 | 20 | 60 |

TABLE II

| Test No. | ASP 1 | Tergitol 15S3 | TPP | K.pyro-phosphate | P.X.S. |
|----------|-------|---------------|-----|------------------|--------|
| 1 | 0 | 40 | 180 | 20 | 108 |
| 2 | 20 | 40 | 180 | 20 | 82 |
| 3 | 40 | 40 | 180 | 20 | 72 |
| 4 | 60 | 40 | 180 | 20 | 70 |
| 5 | 80 | 40 | 180 | 20 | 60 |

EXAMPLE 4

Inhibiting effect of the hydrolysis of TPP by potassium pyrophosphate

Aqueous solutions of sodium tripolyphosphate hydrolyze rapidly to an equilibrium comprising about 2 percent of orthophosphate and about 15 percent of pyrophosphate based on the total phosphate concentration (cf. CHABEREK and MARTELL, "Organic Sequestering Agents," New York, John Wiley Inc., page 304).

To show the inhibiting effect of pyrophosphate on the hydrolysis of TPP, the following detergent composition was prepared:

100 g/liter ASP 4

10 g/liter of TERGITOL 15S3 (secondary C₁₅ alcohol ethoxylated with 7 moles of E.O.)

4 g/liter of potassium diethylene-triamine-pentacetate (Trade Mark VERSENEX 80)

200 g/liter of TPP containing 2.5 percent of sodium pyrophosphate and 1 percent of sodium orthophosphate

20 g/liter of potassium pyrophosphate
50 g/liter of potassium xylene-sulphonate
20 g/liter of potassium sulphate (pH = 8.62)

The said composition was kept at 25°C and the content of tripolyphosphate, pyrophosphate and orthophosphate determined (as percent by weight) at different intervals of time. The results are shown in the following Table:

| Time | Ortho-phosphate | Pyro-phosphate | Tripoly-phosphate |
|---------------|-----------------|----------------|-------------------|
| after 0 day | 0.9 | 11.4 | 87.7 |
| after 11 daYs | 1.0 | 11.3 | 87.7 |
| after 20 daYs | 0.9 | 11.4 | 87.7 |
| after 27 days | 1.0 | 11.8 | 87.2 |
| after 57 days | 1.2 | 12.7 | 86.1 |

It is to be observed that the content of TPP changed from 87.7 percent to 86.1 percent in a period of 57 days, and that the hydrolysis was practically halted by the presence of potassium pyrophosphate.

EXAMPLE 5

Liquid detergent compositions containing surface-active agents of group (d) and (e)

All the detergent compositions contained:

200 g/liter of TPP

20 g/liter of potassium pyrophosphate

20 g/liter of potassium sulphate

150 g/liter of potassium xylene-sulphonate.

Into such compositions surface-active agents of group (d) and (e) were incorporated in the proportions indicated in the following Table.

| | |
|--|---------------|
| d. Potassium C ₁₀ -C ₁₈ alkyl-benzene sulphonate | : 200 g/liter |
| Lauryl-ether-sulphate with from 3.5 moles of E.O. | : 200 g/liter |
| e. C ₁₂ -C ₁₄ alcohol ethoxylated with 3 moles of E.O. | : 100 g/liter |
| Nonylphenol ethoxylated with 6 moles of E.O. | : 100 g/liter |

EXAMPLE 6

Liquid detergent compositions containing surface-active agents of group (c) together with surface-active agents of group (d) or (e)

In the following Table, the concentrations of the various constituents are expressed in g/liter.

| Type (c) | Type (d) or (e) | K or NH ₄ Salt | Solubilizing Agent | K ₄ P ₂ O ₇ | T.P.P. |
|-----------|--|--|--------------------|--|--------|
| 80 ASP 4 | 10 C ₁₅ sec.alcohol-3 E.O. | 50 K ₂ SO ₄ | 70 P.X.S. | 25 | 250 |
| 80 ASP 4 | 10 C ₁₅ sec.alcohol-3 E.O. | 75 K ₂ SO ₄ | 70 P.T.S. | (x) 25 | 250 |
| 50 ASP 2 | 10 C ₁₅ sec.alcohol-7 E.O. | 75 (NH ₄) ₂ SO ₄ | 125 P.X.S. | 25 | 250 |
| 20 ASP 6 | | | | | |
| + | 10 nonylphenol-6 E.O. | 75 KHCO ₃ | 120 P.X.S. | 25 | 250 |
| 30 ASP 2 | | | | | |
| 100 ASP 2 | 20 nonylphenol-6 E.O. | 50 K citrate. H ₂ O | 100 P.X.S. | 20 | 200 |
| 100 ASP 7 | 10 C ₁₂ -C ₁₄ alcohol-6 E.O. | 20 K ₂ SO ₄ | 150 P.X.S. | 20 | 200 |
| 100 ASP 8 | 10 C ₁₂ -C ₁₄ alcohol-6 E.O. | 20 K ₂ SO ₄ | 150 P.X.S. | 20 | 200 |
| 100 ASP 2 | 20 potassium C ₁₈ -C ₁₈ soap | 20 K ₂ SO ₄ | 50 P.X.S. | 20 | 200 |

(x) P.T.S. = potassium-toluene-sulphonate.

EXAMPLE 7

Liquid detergent compositions for heavy duty at high temperature

The efficiency of the heavy duty compositions was tested in a Launder-O-Meter at a temperature of 85°C, for 20 minutes, at a concentration of 5 mls/liter in water of hardness 17°C (French units). Standard artificially soiled swatches were supplied by TEST FABRICS Inc. STANDARD (referred to as TF) and by US TESTING CY STANDARD (referred to as U.S.T). In the said test the percentage of soil removed from the swatches was measured.

In the following Table, Tests 1 to 3 were effected with compositions according to the invention, all of which contained:

100 g/l of ASP 2

6 g/l of tetrasodium EDTA

2 g/l of polyvinylpyrrolidone

100 g/l of potassium xylene-sulphonate

20 g/l of K₄P₂O₇, and

200 g/l of TPP.

In addition, the composition for test No. 1 contained 20 g/l of nonylphenol ethoxylated with 6 E.O., 50 g/l of boric acid and 12.5 g/l of KOH; the composition for test No. 2 contained 20 g/l of nonylphenol ethoxylated with 6 E.O. and 50 g/l of potassium citrate; the composition for test No. 3 contained 20 g/l of C₁₆-C₂₀ alcohol ethoxylated with 6 E.O. and 50 g. of KHCO₃.

Tests No. 4 and No. 5 were carried out with commercial "heavy duty" powders, namely "ALL" (No. 4) and "PRODIXAN" (No. 5), respectively, used in a proportion of 5 g/liter.

| Test No. | TF | U.S.T. |
|----------|------|--------|
| 1 | 64.7 | 18.1 |
| 2 | 64.5 | 18.7 |
| 3 | 65.1 | 18.0 |
| 4 | 54.9 | 15.6 |
| 5 | 56.0 | 16.9 |

It is to be noted that tests No. 1 to 3 were superior to tests No. 4 and 5.

EXAMPLE 8

Demonstration of the greater concentration of TPP in liquid detergent compositions

The test carried out in this Example is the same as that of Example 7, using similar swatches TF and U.S.T. and in the comparison of the use of washing powders "ALL" and "PRODIXAN." The water used had a hardness of 40° in French units.

Tests No. 1 to 5 were carried out with liquid compositions according to the invention containing increasing proportions of TPP, namely: 0, 50, 100, 150 and 200 (g/liter), the compositions containing also the following:

100 g/l of ASP 2

20 g/l of nonylphenol ethoxylated with 6 E.O.

20 g/l of polyvinylpyrrolidone

6 g/l of tetrasodium EDTA

100 g/l of potassium xylene-sulphonate

20 g/l of K₄P₂O₇ and

20 g/l of K₂SO₄.

Tests No. 6 and 7 were carried out with "ALL" and "PRODIXAN"

| Test No. | TF | U.S.T. |
|----------|------|--------|
| 1 | 23.2 | 3.7 |
| 2 | 32.2 | 5.5 |

| | | |
|---|------|------|
| 3 | 53.9 | 7.4 |
| 4 | 64.6 | 11.5 |
| 5 | 67.6 | 16.0 |
| 6 | 52.7 | 14.6 |
| 7 | 56.2 | 15.7 |

The Table clearly shows the effectiveness of the compositions with increasing TPP content.

EXAMPLE 9

Liquid detergent compositions for heavy duty at low temperature

The compositions are expressed in g./liter:

| | Composi- tion I | Composi- tion II |
|--|--------------------|---------------------|
| ASP 3 | 50 | 50 |
| nonylphenol ethoxylated with 6 moles of E.O. | 40 | — |
| C ₁₁ -C ₁₈ secondary alcohol ethoxylated with 3 moles E.O. | — | 25 |
| C ₁₁ -C ₁₈ secondary alcohol ethoxylated with 7 moles E.O. | — | 25 |
| pentasodium DTPA | 4 | 4 |
| polyvinyl pyrrolidone | 1 | 1 |
| potassium xylene-sulphonate | 100 | 100 |
| K ₄ P ₂ O ₇ | 20 | 20 |
| K ₂ SO ₄ | 20 | 20 |
| TPP | 180 | 180 |

EXAMPLE 10

Liquid detergent compositions for light duty

The tests were carried out in a Tergometer for 10 minutes at a temperature of 40°C, using 5 mls. of detergent composition per liter of water having a hardness of 17° French units.

Artificially soiled swatches were used marketed by the firm TESTFABRICS Inc., U.S.A. These consisted of nylon (N), a 65/35 polyester/cotton (P) and wool (L).

Four compositions according to the invention were used, each containing:

- 60 g/l of ASP 2
- 6 g/l of tetrasodium EDTA
- 90 g/l of potassium xylene-sulphonate
- 1 g/l of polyvinyl pyrrolidone
- 20 g/l of K₂SO₄
- 20 g/l of K₄P₂O₇
- 200 g/l of TPP

but being different from each other by the presence of the following compounds:

Composition for Test No. 1

20 g/liter of C₁₅ secondary alcohol ethoxylated with 3 moles of E.O.

20 g/liter of C₁₅ secondary alcohol ethoxylated with 7 moles of E.O.

20 g/liter of the diethanolamide of ethoxylated coco fatty acids

Composition for Text No. 2

40 g/liter of nonylphenol ethoxylated with 6 moles of E.O.

20 g/liter of the monoethanolamide of coco fatty acids.

Composition for Test No. 3

40 g/liter of nonylphenol ethoxylated with 6 moles of E.O.

Composition for Test No. 4

40 g/liter of nonylphenol ethoxylated with 6 moles of E.O.

10 g/liter of the diethanolamide of lauric acid

10 g/liter of lauryl-ether-sulphate with 2.5 moles of E.O.

Test No.5 and No.6 were carried out with the commercial light duty liquids "OSA" (No. 5) and "SOLILAINE" (No.6) respectively, both used in the tests at a concentration of 5 ml/liter.

The results obtained are shown in the following Table:

| Test No. | N | P | L |
|----------|------|------|------|
| 1 | 80.3 | 36.2 | 90.1 |
| 2 | 80.1 | 41.1 | 92.9 |
| 3 | 75.5 | 41.8 | 92.3 |
| 4 | 81.7 | 40.0 | 76.4 |
| 5 | 71.1 | 23.5 | 25.2 |
| 6 | 64.6 | 30.9 | 65.9 |

The superiority and polyvalence of the compositions according to the invention (Test Nos. 1 to 4) are shown despite the fact that the commercial compositions (Test No. 5 and 6) contained greater portions of surface-active material (more than 25 percent). The compositions according to the invention are as well suited for hand washing as for machine washing.

I claim:

1. A homogeneous aqueous solution consisting essentially of water and (a) from 14 to 35 percent by weight of sodium tripolyphosphate and (b) from 0.1 to 50 percent by weight of at least one salt selected from the group consisting of potassium and ammonium sulfate, chloride, nitrate, carbonate bicarbonate, orthoborate, metaborate, tetraborate perborate, orthophosphate, metaphosphate, pyrophosphate, maleate, adipate, aconitate, citrate, tartrate, succinate, ethylenediaminetetraacetate, nitrilotriacetate and diethylenetriaminepentaacetate.

2. A homogeneous liquid detergent composition in the form of an aqueous solution consisting essentially of water and

a. from 14 to 35 percent by weight of sodium tripolyphosphate,

b. from 0.1 to 50 percent by weight of at least one salt selected from the group consisting of potassium and ammonium sulfate, chloride, nitrate, carbonate, bicarbonate, orthoborate, metaborate, tetraborate, perborate, orthophosphate, metaphosphate, pyrophosphate, maleate, adipate, aconitate, citrate, tartrate, succinate, ethylenediaminetetraacetate, nitrilotriacetate and diethylenetriaminepentaacetate,

c. from 0 to 35 percent by weight of at least one sodium, potassium or triethanolamine salt of a sulfopolycarboxylic acid ester with at least one hydroxy-containing non-ionic surface-active agent selected from the group consisting of aliphatic alcohols containing from eight to 22 carbon atoms ethoxylated with from 1 to 50 moles of ethylene oxide per mole of alcohol, and alkylphenols containing six to 12 carbon atoms in the alkyl chain and ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alkylphenol, said sulfopolycarboxylic acid being selected from the group consisting of sulfosuccinic acid, sulfotriballylic acid and the sulfopolycarboxylic acid obtained by sulfonating and acidifying the pyrolysis product of calcium citrate.

d. from 0 to 20 percent by weight of at least one anionic surface-active agent selected from the group consisting of fatty acid soaps containing from 10 to 22 carbon atoms, alkyl sulfonates containing from 8 to 25 carbon atoms, alkylbenzene

sulfonates containing from 10 to 16 carbon atoms in the alkyl group, alkyl sulfates containing from eight to 18 carbon atoms, alkyl polyoxyethylene ether sulfates and alkylaryl polyoxyethylene ether sulfates, the alkyl group of which contains eight to 18 carbon atoms and the polyoxyethylene group of which contains from 1 to 4 ethylene oxide units,

- e. from 0 to 15 percent by weight of at least one non-ionic surface-active agent selected from the group consisting of alkylphenols containing from six to 12 carbon atoms in the alkyl chain and ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alkylphenol, aliphatic alcohols containing from eight to 22 carbon atoms ethoxylated with from 1 to 50 moles of ethylene oxide per mole of alcohol, fatty acid ethanalamides and ethoxylated fatty acid ethanalamides, and
- f. from 0 to 20 percent by weight of at least one solubilizing agent selected from the group consisting of potassium xylene sulfonate, potassium toluene sulfonate and potassium cumene sulfonate, at least one of compounds (c), (d) and (e) being present.

3. A composition according to claim 2, wherein the salt (b) potassium pyrophosphate is in a proportion of from 5 to 25 percent by weight based on the amount of sodium tripolyphosphate.

4. A composition according to claim 2, wherein the salt (c) is a potassium salt.

5. A composition according to claim 2, wherein the anionic surface-active agent (d) is a potassium salt.

6. A composition according to claim 2, wherein salt (c) is present in a proportion of from 1 to 20 percent by weight of the total composition.

7. A composition according to claim 2, wherein at least one of compounds (d) and (e) is present, compound (d) in a proportion of from 1 to 15 percent by weight and compound (e) in a proportion of from 1 to 10 percent by weight of the total composition, and solubilizing agent (f) is present in a proportion of from 1 to 12 percent by weight of the total composition.

8. A composition according to claim 2, wherein salt (c) is present in a proportion of from 1 to 20 percent by weight of the total composition and at least one of compounds (d) and (e) is present, compound (d) in a proportion of from 1 to 15 percent by weight and compound (e) in a proportion of from 1 to 10 percent by weight of the total composition, and solubilizing agent (f) is present in a proportion of from 1 to 12 percent by weight of the total composition.

9. A homogeneous liquid detergent composition in the form of an aqueous solution consisting essentially of water and

- a. from 18 to 28 percent by weight of sodium tripolyphosphate,
- b. from 1 to 10 percent by weight of at least one salt selected from the group consisting of potassium and ammonium sulfate, chloride, nitrate, carbonate, bicarbonate, orthoborate, metaborate, tetraborate, perborate, orthophosphate, metaphosphate, pyrophosphate, maleate, adipate, aconitate, citrate, tartrate, succinate, ethylenediaminetetraacetate, nitrilotriacetate and diethylenetriaminepentaacetate, and
- c. from 1 to 20 percent by weight of at least one sodium, potassium or triethanolamine salt of a sulfocarboxylic acid ester with at least one hydroxy-

containing non-ionic surface-active agent selected from the group consisting of aliphatic alcohols containing from eight to 22 carbon atoms ethoxylated with from 1 to 50 moles of ethylene oxide per mole of alcohol, and alkylphenols containing six to 12 carbon atoms in the alkyl chain and ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alkylphenol, said sulfopolycarboxylic acid being selected from the group consisting of sulfosuccinic acid, sulfotricarballylic acid and the sulfopolycarboxylic acid obtained by sulfonating and acidifying the pyrolysis product of calcium citrate.

10. A composition according to claim 9, wherein the salt (b) potassium pyrophosphate is in a proportion of from 5 to 25 percent by weight based on the amount of sodium tripolyphosphate.

11. A homogeneous liquid detergent composition in the form of an aqueous solution consisting essentially of water and

- a. from 18 to 28 percent by weight of sodium tripolyphosphate,
- b. from 1 to 10 percent by weight of at least one salt selected from the group consisting of potassium and ammonium sulfate, chloride, nitrate, carbonate, bicarbonate, orthoborate, metaborate, tetraborate, perborate, orthophosphate, metaphosphate, pyrophosphate, maleate, adipate, aconitate, citrate, tartrate, succinate, ethylenediaminetetraacetate, nitrilotriacetate and diethylenetriaminepentaacetate,
- c. from 1 to 20 percent by weight of at least one sodium, potassium or triethanolamine salt of a sulfopolycarboxylic acid ester with at least one hydroxy-containing non-ionic surface-active agent selected from the group consisting of aliphatic alcohols containing from eight to 22 carbon atoms ethoxylated with from 1 to 50 moles of ethylene oxide per mole of alcohol, and alkylphenols containing six to 12 carbon atoms in the alkyl chain and ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alkylphenol, said sulfopolycarboxylic acid being selected from the group consisting of sulfosuccinic acid, sulfotricarballylic acid and the sulfopolycarboxylic acid obtained by sulfonating and acidifying the pyrolysis product of calcium citrate, and
- d. from 1 to 15 percent by weight of at least one anionic surface-active agent selected from the group consisting of fatty acid soaps containing from 10 to 22 carbon atoms, alkyl sulfonates containing from eight to 25 carbon atoms, alkylbenzene sulfonates containing from 10 to 16 carbon atoms in the alkyl group, alkyl sulfates containing from eight to 18 carbon atoms, alkyl polyoxyethylene ether sulfates and alkylaryl polyoxyethylene ether sulfates, the alkyl group of which contains eight to 18 carbon atoms and the polyoxyethylene group of which contains from 1 to 4 ethylene oxide units, and/or
- e. from 1 to 10 percent by weight of at least one non-ionic surface-active agent selected from the group consisting of alkylphenols containing from six to 12 carbon atoms in the alkyl chain and ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alkylphenol, aliphatic alcohols containing from eight to 22 carbon atoms ethoxylated with from 1 to 50 moles of ethylene oxide per mole of alcohol, fatty acid ethanalamides and ethoxylated fatty

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acid ethanolamides, and
f. from 1 to 12 percent by weight of at least one solubilizing agent selected from the group consisting of potassium xylene sulfonate, potassium toluene sulfonate and potassium cumene sulfonate.

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12. A composition according to claim 11, wherein the salt (b) potassium pyrophosphate is in a proportion of from 5 to 25 percent by weight based on the amount of sodium tripolyphosphate.

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