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LIQUID DETERGENT COMPOSITIONS

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This invention relates to liquid detergent compositions. This application is a continuation-in-part of my copending application Serial No. 396,313 filed December 4, 1953, and now abandoned.

The improved compositions of this invention provide highly concentrated solutions of an organic wetting agent and a phosphate builder. The concentrated solution is very stable and will not separate into phases or deposit solids over long periods of standing. Stability is achieved by the use of isoamyl acid phosphate coupling agents which increase the mutual solubilities of the wetting agent and builder in aqueous solution, thereby permitting the production of a more concentrated product.

Many attempts have been made to produce an ideal liquid detergent containing a wetting agent and a phosphate builder but only limited success has been met. Inherent disadvantages in this type of composition include incompatability of the components, relative insolubility of some of the components and instability of the composition to temperature changes. Consequently, the solutions are usually turbid or heterogeneous, making them commercially unsatisfactory.

A variety of methods have been used in an attempt to overcome these difficulties. Thus some liquid detergents are in the form of dilute solutions ready for use full strength. This type of product eliminates the solubility problem. Other detergents use a liquid hydrocarbon for a base to avoid solubility problems; others limit themselves to a specific wetting agent or builder which has unique solubility characteristics. All of these methods of overcoming specific difficulties, however, have done so at the expense of either versatility, economy or quality.

Thus the ideal liquid detergent should be a concentrated solution containing an excellent wetting agent in combination with an excellent builder. Preferably there should be a wide choice among wetting agents and builders so that a variety of specific detergents having the same general composition could be prepared for special purposes.

I have now found that a concentrated, stable solution of a variety of organic wetting agents and phosphate builders may be produced by using an isoamyl acid phosphate as a coupling or solubilizing agent. This solution does not settle into layers upon standing. It may be cooled within usual temperature limits with only slight clouding and will regain its original clarity when warmed to room temperature. It may be used for all general household purposes and is particularly good for laundering wherein it has excellent cleansing and detergency qualities.

The isoamyl acid phosphate coupling agents which I have discovered appear to be unique in their action. Similar propyl, butyl and octyl compounds for instance do not appear to work in this invention. Either the ortho or pyro form of the acid phosphate is suitable. These may not be specific compounds, but when formed as shown in the following equations the products produced give analyses which indicate that nearly a pure compound is produced.

The mono-di-isoamyl acid orthophosphate may be prepared as follows:

$$3(\text{i-AmOH}) + P_2O_5 \rightarrow (\text{iAmO})(HO)_2PO.\ (\text{i-AmO})_2(HO)PO$$

The di-isoamyl acid pyrophosphate may be prepared as follows:

$$2(\text{i-AmOH}) + P_2O_5 \rightarrow (\text{i-Am})_2H_2P_2O_7$$

The simple mono-isoamyl-diacid orthophosphate and di-isoamyl acid orthophosphate are also satisfactory for this invention. The mono-di-isoamyl acid orthophosphate described above is in effect an equimolar mixture of these two compounds.

The isoamyl alcohol used in making these compounds is preferably the commercial grade material which is commonly known as fusel oil. More refined grades are suitable but are uneconomical.

The value of these compounds lies in the fact that they appear to be uniquely able to assist the formation of a concentrated solution of an organic wetting agent and a phosphate builder.

Normally in a concentrated solution containing these two ingredients the phosphate has a tendency to salt out the wetting agent. This prevents the formation of a concentrated solution and also causes much difficulty due to phase separation, etc. In addition to the coupling effect, the amyl acid phosphates also enhance the washing qualities of the solution since they are in themselves good wetting agents.

The preferred class of organic wetting agents for use in this invention are the higher alkyl aryl alkali metal sulfonates; of these, Nacconol NRSF is especially preferred. However, other anionic synthetic detergents, such as Nacconol NR, Oronite D–40, Ninex 21, Igepon T–77, and Ultrawet K, may also be used.

In addition, nonionic organic wetting agents are also solubilized by the amyl acid phosphates. For example, among the commercially available nonionic wetting agents which have been found effective are Ninol AA62 and Alrosol.

Nacconol NR and Nacconol NRSF are synthetic anionic surface active detergents of the higher alkyl aromatic sulfonate type prepared from a starting material obtained by the Friedel-Crafts condensation of a mono-chlorinated kerosene fraction with benzene at about 35–50 degrees C. using aluminum chloride as a catalyst, the kerosene fraction refined from Pennsylvania crude having a high aniline point, a boiling range of 200–300 degrees C. and an average molecular weight corresponding to a saturated aliphatic hydrocarbon of about 14 carbon atoms. The alkyl aryl condensation product is separated from the condensation reaction and sulfonated with sulfuric acid monohydrate or oleum at temperatures under 60 degrees C. The neutralized dried sodium sulfonate containing about 10% or less of sulfuric acid in the form of inorganic salt is the Nacconol NRSF, the "low-salt content" grade, while the product containing about 60% of inorganic salt, mainly sodium sulfate, is Nacconol NR.

Oronite D–40 and Ultrawet K are synthetic anionic surface active detergents of the higher alkyl aromatic sulfonate types as are the Nacconols referred to above, except that instead of benzene as the aromatic hydrocarbon employed in the Friedel-Crafts alkylation condensation, the aromatic nucleus is furnished by a mixture of lower homologues of benzene such as toluene and xylene, and lesser amounts of cumene. Ultrawet K contains about 85% of the active detergent agent in the form of the sodium sulfonate of the alkyl aryl condensation product.

Oronite D–40 is like Nacconol NR in being a dry product containing about 40% of the active detergent

agent, the remainder being inorganic salt, mainly sodium sulfate.

Igepon T–77 is sodium N-methyl-N-oleoyl taurate.

Ninol AA62 is lauric diethanol amide which may be produced in the manner set forth in U.S. Patent 2,089,212, whereas Ninex 21 contains approximately equal parts by weight of lauric diethanol amide plus a triethanol amine salt of dodecyl benzene sulfonate.

Alrosol is a coconut oil diethanol amide which may be produced in the manner set forth in U.S. Patent 2,089,212.

Phosphate builders are well known for their ability to enhance the cleansing action of soaps and wetting agents. The phosphate builders which are suitable include the well known alkali metal polyphosphate salts such as tetrasodium pyrophosphate, tetrapotassium pyrophosphate, sodium tripolyphosphate, potassium tripolyphosphate, sodium hexametaphosphate, ammonium metaphosphate, and the like. Orthophosphates such as disodium phosphate, trisodium phosphate, monopotassium phosphate, and the like are also compatible when the isoamyl acid phosphate coupling agent is used.

The preferred phosphate builder for use in this invention is "Victamide." This compound, as described in U.S. Patent 2,122,122 is a substantially neutral compound consisting of a nitrogen-phosphorus complex, resulting from heating a reaction product of P_2O_5 and anhydrous ammonia gas or liquid at a temperature of at least about 150° C. in the presence of excess anhydrous ammonia to produce a condensation reaction, said compound having an atomic ratio of nitrogen to phosphorus of less than 1½ to 1 with the ammonium nitrogen being from 60–80% of the total nitrogen and containing substantially no water of constitution. For example, the product may be produced by vapor phase reaction between the ingredients under anhydrous conditions. In this reaction phosphoric anhydride and anhydrous ammonia are heated at a temperature of at least 150° C. in an excess of ammonia gas for a period sufficient to form a product, having a total nitrogen to phosphorus mole ratio between 1 and 1.5, with the ammonium nitrogen content being from 60–80% of the total nitrogen. The product will normally have a pH value in a 1% solution of about 5.5 to 6.0, and a ratio of N to P of approximately 1.25, a P_2O_5 content of approximately 76.1%, a total NH_3 of about 22.4%, and nuclear or amide nitrogen calculated as NH_3 of about 7.0%. Such analysis is typical and is not intended to set the exact specification of the reaction product to be employed in the present invention. Various structures have been proposed for this reaction product of P_2O_5 and NH_3 although the structure has never been definitely ascertained. It appears quite certain, however, that P—O—P or P—N—P linkages or both are present in the final product. Since the P—O—P linkage is commonly associated with polyphosphates, it is thought that "Victamide" as described above may properly be classified as such. For purposes of this invention the unit ≡P—X—P≡, where X is a member of the class consisting of O and N is intended to include "Victamide" and the common polyphosphates. "Victamide" may be dissolved in water to form solutions of 50–60% concentration although solutions of approximately 30% concentration are preferred for use in this invention.

In addition to the three major components of these liquid detergents certain well-known special additives may be incorporated to produce specially desired results. These additives may include foam stabilizers, whitening agents, dispersants, and the like.

The general procedure followed in producing these liquid detergents is to first form clear, water solutions of the phosphate builder. In the case of the preferred "Victamide" this may be accomplished by allowing the solution to stand overnight at room temperature or the process may be hastened by heating at 60–90° C. for approximately one-half hour. As will be seen in the following examples, solutions varying from 15% up to saturation are used for the various other phosphate salts. These are produced by well-known methods.

The isoamyl acid phosphate coupling agent is then added to the phosphate builder solution which usually results in a two phase mixture. The mixture is then made homogeneous by adjusting the pH with an aqueous solution of a base. Sodium hydroxide is commonly used to effect maximum solubility although ammonium hydroxide, well-known amines, such as triethylamine, triethanolamine, and the like, may be used. A wide range of pH values may be used without adversely affecting the product. Solutions ranging from pH 5 to 10 have been used in certain cases. Generally this pH adjustment is made by adding an approximately 20% sodium hydroxide solution until a clear detergent solution results. The total amount of caustic is generally less than 7% of the composition, but this is not critical and depends on the desired pH.

My clear, homogeneous, concentrated aqueous liquid detergent compositions may contain 35 to 75 parts by weight water, 5 to 30 parts by weight of a water-soluble inorganic phosphate builder, 5 to 20 parts by weight wetting agent from the group consisting of nonsoap synthetic anionic organic wetting agents and synthetic alkylolamide nonionic organic wetting agents, and 2–20 parts by weight of a coupling agent from the group consisting of isoamyl acid orthophosphate and isoamyl acid pyrophosphate, said composition having a pH of from 5 to 10.

The following compositions illustrate the wide range of different phosphate builders and wetting agents which can be used with the isoamyl acid phosphate coupling agents.

COMPOSITION 1

	Percent
"Victamide"	20
Mono-di-isoamyl acid orthophosphate	4.5
"Nacconol NRSF"	10.0
NaOH	0.7
Water	64.8
	100.0

The pH of this composition was 5.1. It was possible to raise this clear through the range up to a pH of 9.5 by increasing the NaOH to 5.4% and reducing the amount of water accordingly.

COMPOSITION 2

	Percent
Tetrasodium pyrophosphate	7.3
Mono-di-isoamyl acid orthophosphate	13.1
"Nacconol NRSF"	10.9
NaOH	0.7
Water	68.0
	100.0

COMPOSITION 3

	Percent
Tetrapotassium pyrophosphate	35.7
Mono-di-isoamyl acid orthophosphate	12.8
"Nacconol NRSF"	10.7
NaOH	1.0
Water	39.8
	100.0

COMPOSITION 4

Sodium tripolyphosphate	10.6
Mono-di-isoamyl acid orthophosphate	16.9
"Nacconol NRSF"	10.6
NaOH	0.4
Water	61.5
	100.0

COMPOSITION 5

	Grams
30% potassium tripolyphosphate soln	100
Di-isoamyl acid pyrophosphate	20
"Nacconol NRSF"	5

20% NaOH solution to a pH of 6 gave a clear solution.

COMPOSITION 6

15% ammonium metaphosphate solution	100
Mono-di-isoamyl acid orthophosphate	6
"Nacconol NRSF"	5.5

20% NaOH solution to make a clear soln.

COMPOSITION 7

15% sodium hexametaphosphate soln	100
Mono-di-isoamyl acid orthophosphate	6
"Nacconol NRSF"	10

20% NaOH solution to make a clear soln.

COMPOSITION 8

30% Victamide solution	100
Mono-di-isoamyl acid orthophosphate	6
"Ultrawet K"	6

(No NaOH was needed.)

COMPOSITION 9

40% "Victamide" solution	100
Mono-di-isoamyl acid orthophosphate	15
"Oronite D–40"	20
22% NaOH soln to make a clear soln	65

COMPOSITION 10

	Percent
Trisodium phosphate.$12H_2O$	12.0
Mono-di-isoamyl acid orthophosphate	7.5
"Nacconol NRSF"	10.0
Water	70.5
	100.0

COMPOSITION 11

"Victamide"	20
Mono-di-isoamyl acid orthophosphate	7.5
"Ninex 21"	10.0
Water and caustic	62.5
	100.0

COMPOSITION 12

"Victamide"	20
Mono-di-isoamyl acid orthophosphate	7.5
"Ninol AA62"	10.0
Water and caustic	62.5
	100.0

COMPOSITION 13

"Victamide"	20
Mono-di-isoamyl acid orthophosphate	7.5
"Alrosol"	10.0
Water and caustic	62.5
	100.0

In the following washing tests four examples of liquid detergents representative of the present invention are compared with two well-known commercial liquid detergents. The samples tested had the following compositions.

Sample No. 1

	Percent
"Victamide"	21.6
Mono-di-isoamyl acid orthophosphate	4.3
"Nacconol NRSF"	14.4
Water and caustic	59.7
	100.0

Sample No. 2

Tetrapotassium pyrophosphate	20.7
Mono-di-isoamyl acid orthophosphate	4.1
"Nacconol NRSF"	6.2
Water	69.0
	100.0

Sample No. 3

Tetrasodium pyrophosphate	7.0
Mono-di-isoamyl acid orthophosphate	12.5
"Nacconol NRSF"	10.4
Water and caustic	70.1
	100.0

Sample No. 4

Sodium tripolyphosphate	11.0
Mono-di-isoamyl acid orthophosphate	4.4
"Nacconol NRSF"	11.0
Water and caustic	73.6
	100.0

Sample No. 5

A commercial liquid detergent comprising approximately—

60% triethanolamine salt of lauryl acid sulfate
20% alcohol
20% water

Sample No. 6

A commercial liquid nonionic detergent comprising approximately an 83% active solution of an ethylene oxide condensation product of an alkyl phenol.

The comparative detergencies of the above were tested by washing a standard soiled cloth in a launderometer. Synthetic hard water was prepared by dissolving calcium and magnesium nitrates in a 2:1 ratio. All detergents were used in an amount equivalent to 0.3% concentration calculated on the basis of the dry active ingredient.

Detergency is measured by the percent reflectance value which is a measure of light reflected in a reflectometer as compared to 100% for an unsoiled white cloth. Each reflectance value is the average of four washes.

TABLE I

[Detergency tests at 120° F.]

Sample No.	Active Conc., Percent	Total Conc., Percent	Water Hardness			
			150 p.p.m.		300 p.p.m.	
			pH	Reflectance	pH	Reflectance
1	0.3	0.75	6.0	72	5.6	68
2	0.3	1.0	6.8	70	6.6	66
3	0.3	1.0	8.3	60	8.0	47
4	0.3	1.0	8.3	59	8.0	47
5	0.3	0.5	6.8	52	7.1	41

TABLE II

[Detergency tests at 150° F.]

Sample No.	Active Conc., Percent	Total Conc., Percent	Water Hardness			
			150 p.p.m.		300 p.p.m.	
			pH	Reflectance	pH	Reflectance
1	0.3	0.75	6.1	69	5.7	68
2	0.3	1.0	6.8	69	6.7	67
3	0.3	1.0	8.4	67	8.2	52
4	0.3	1.0	8.4	68	8.2	52
6	0.3	0.375	7.8	44	7.8	41

As can be seen from the above results, Samples 1 and 2

are noticeably superior to Samples 5 and 6 at water hardnesses of both 150 and 300 p.p.m. Samples 3 and 4 are in all cases better than the commercial detergents although not to the extent of Samples 1 and 2.

Compositions similar to Samples 1 and 2 after aging have been found to retain this excellent degree of detergency for at least six months as shown by tests similar to those shown above.

Thus although Samples 5 and 6 contain a higher concentration of a single active ingredient than do Samples 1 through 4, the detergency tests show that Samples 1 to 4 produce better washing results. This is possible since the isoamyl acid phosphate coupling agent provides a means of combining a wetting agent and a phosphate builder in a concentrated liquid solution wherein the advantage of the well-known synergistic detergency effect of the combination is preserved. In other words, the unique property of the isoamyl phosphate enables me to produce a detergent composition of superior quality having all of the qualities and advantages desired in a concentrated liquid form.

All percentages and relative amounts given herein are by weight.

Having described my invention as related to the embodiments described herein, it is my intention that the invention be not limited by any of the details of description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

I claim:

1. A clear, homogeneous, concentrated aqueous liquid detergent composition comprising 35 to 75 parts by weight water, 5 to 30 parts by weight of a water-soluble inorganic phosphate builder, 5 to 20 parts by weight wetting agent from the group consisting of nonsoap synthetic anionic organic wetting agents and synthetic alkylolamide nonionic organic wetting agents, and a solubilizing amount of a coupling agent from the group consisting of isoamyl acid orthophosphate and isoamyl acid pyrophosphate, said composition having a pH of from 5 to 10.

2. The composition of claim 1 wherein the synthetic anionic wetting agent is a higher alkyl aryl alkali metal sulfonate.

3. The composition of claim 1 wherein the water-soluble inorganic phosphate builder is a polyphosphate.

4. The composition of claim 1 wherein the water-soluble inorganic phosphate builder is a substantially neutral compound consisting of a nitrogen-phosphorus complex resulting from heating a reaction product of P_2O_5 and anhydrous ammonia at a temperature of at least about 150 degrees C. in the presence of excess anhydrous ammonia to produce a condensation reaction, said compound having an atomic ratio of nitrogen to phosphorus of less than 1½ to 1 with the ammonium nitrogen being from 60–80% of the total nitrogen and containing substantially no water of constitution.

5. The composition of claim 1 wherein the coupling agent consists essentially of mono-di-isoamyl acid orthophosphate.

6. A clear, homogeneous, concentrated aqueous liquid detergent composition comprising 35 to 75 parts by weight water, 5 to 30 parts by weight of a water-soluble inorganic phosphate builder, 5 to 20 parts by weight wetting agent from the group consisting of nonsoap synthetic anionic organic wetting agents and synthetic alkylolamide nonionic organic wetting agents, and 2–20 parts by weight of a coupling agent from the group consisting of isoamyl acid orthophosphate and isoamyl acid pyrophosphate, said composition having a pH of from 5 to 10.

7. The composition of claim 6 wherein the synthetic anionic wetting agent is a higher alkyl aryl alkali metal sulfonate.

8. The composition of claim 6 wherein the water-soluble inorganic phosphate builder is a substantially neutral compound consisting of a nitrogen-phosphorus complex resulting from heating a reaction product of P_2O_5 and anhydrous ammonia at a temperature of at least about 150 degrees C. in the presence of excess anhydrous ammonia to produce a condensation reaction, said compound having an atomic ratio of nitrogen to phosphorus of less than 1½ to 1 with the ammonium nitrogen being from 60–80% of the total nitrogen and containing substantially no water of constitution.

9. The composition of claim 6 wherein the synthetic anionic wetting agent is a higher alkyl aryl alkali metal sulfonate and the water-soluble inorganic phosphate builder is a substantially neutral compound consisting of a nitrogen-phosphorus complex resulting from heating a reaction product of P_2O_5 and anhydrous ammonia at a temperature of at least about 150 degrees C. in the presence of excess anhydrous ammonia to produce a condensation reaction, said compound having an atomic ratio of nitrogen to phosphorus of less than 1½ to 1 with the ammonium nitrogen being from 60–80% of the total nitrogen and containing substantially no water of constitution.

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