Dishwasher detergent composition.

A liquid dishwasher detergent emulsion provided by this invention has high alkalinity, high levels of sequestrant and high temperature stability. The detergent emulsion comprises:

i) 4 to 25% w/w of an alkali metal hydroxide suitable for use in a dishwasher;
ii) 0.2 to 5% w/w of a low foaming free non-ionic surfactant;
iii) 0.5 to 3% w/w of a polyacrylic acid suitable for enhancing sheeting action on non-porous surfaces;
iv) 15 to 30% w/w of a potassium polyphosphate sequestering composition enriched in tripolyphosphate and comprising minimal amounts of ortho and long forms of polyphosphates to facilitate thereby solubility of said potassium polyphosphate in water;
v) 2 to 6% w/w of a polymeric emulsion stabilizer for said free nonionic surfactant, the polymeric emulsion stabilizer being a chemically associated polycarboxylic acid polymer and a nonionic surfactant formed by polymerization of said nonionic surfactant with a polymerizable reactant selected from the group consisting of acrylic acid, polyacrylic acid, copolymers of acrylic acid and an ethylenically unsaturated polycarboxylic acid or an anhydride thereof, copolymers of ethylenically unsaturated polycarboxylic acid or anhydride thereof with a non-carboxy containing ethylenically unsaturated monomer, said nonionic surfactant and said reactant being polymerized in an aqueous media;
v) 0 to 15% w/w of a sequestering agent to enhance hard water sequestering characteristics of said potassium polyphosphate; and
vii) water to make up the balance of composition to 100% w/w.
This invention relates to liquid dishwasher detergent emulsions and more particularly detergent emulsion having high alkalinity, high levels of sequestrant and high temperature stability.

Dishwasher detergent compositions are commonly provided in the form of a solid or a liquid which may be a slurry, an emulsion or a solution. Such detergents are formulated for use in household, industrial or institutional type dishwashers. It is appreciated that formulations for household dishwashers are of relatively low alkalinity with suitable levels of surfactant and various types of sheeting agents. However with industrial and institutional type dishwashers, the formulations are considerably more concentrated in the active ingredients to achieve dishwashing cycles within the one to two minute range. Solids are the most suitable medium to incorporate high levels of active ingredients, because liquid stability is not of concern. Very high levels of alkalinity and surfactant can be incorporated into solid detergents. However, dissolution rates can be a problem particularly with shorter cycle machines. Granular powders are suited for better dissolution, but inherently include problems with respect to dispensing within institutional dishwashing machines. Metering of powders can be done by machine or manually. The powders are not always properly dispensed within the machine for proper cleaning effectiveness during the short cycle of the machine. Systems designed to meter powders are very expensive and can only be justified for use on large industrial or institutional dishwashing machines.

Liquid forms of detergent detergents are preferred from the standpoint of metering the necessary dose of detergent into the machine for each cycle and for their rates of dissolution in wash water. The problem with liquid dishwasher detergents is, however, long term stability. There is considerable difficulty incorporating high levels of alkalinity and surfactant in a liquid detergent while maintaining flowability and composition concentration uniformity. One form of liquid detergent which is popular and has high levels of alkalinity and surfactants is the slurry. Examples of slurries are disclosed in United States patents 4,215,004 and 4,597,889. Partially esterified maleic acid copolymers are used to stabilize the slurries containing solid particulate forms of surfactant and/or alkalinity agents or other active agents. Slurries can, however, be too viscous for dispensing into institutional type dishwashing machines. Elaborate electronic pumping and metering system are required to ensure a consistent dosing of the required amount of dishwasher detergent liquid into the machine for each cycle.

An aqueous built liquid detergent is disclosed in United States patent 4,082,684. The detergent includes a maleic anhydride copolymer partially esterified with a nonionic surfactant and sodium tripolyphosphate as the sequestrant. It has been found, however, that the esterified maleic anhydride polymers are not sufficiently effective to stabilize liquid compositions having high levels of alkalinity, surfactant and sequestrant, particularly nonionic surfactants. In this patent, the formulation is at a pH of 11 which is adjusted by use of potassium hydroxide. The potassium hydroxide is used to neutralize the maleic anhydride polymer and the fatty acid soap. The aqueous built detergent composition is of fairly high viscosity in the range of 550 to 1000 centipoise.

A stable detergent emulsion including a nonionic surfactant is disclosed in applicants, United States patent 4,826,618 and co-pending U.S. application S.N. 078,893 filed July 29, 1987, the disclosures of which are incorporated herein by reference. Emulsions are preferred for dispensing in various types of dishwashers because of their flowability and dissolution rates. The emulsion of this patent is stabilized by the use of a polymeric phase stabilizer. The stabilizer is prepared by the polymerization of an unsaturated acrylic acid or a short chain polycarboxylate in an aqueous alkaline media in the presence of a nonionic surfactant. Suitable amounts of unsaturated acrylic acid or short chain polycarboxylate are admixed in aqueous media together with a nonionic surfactant and a suitable chemical initiator to begin and maintain polymerization reaction. Hence the nonionic surfactant is incorporated into the polymer chain as differentiated from maleic acid copolymers which are partially esterified with a nonionic surfactant. Although the compositions of that patent are suitable for use in dishwashers, the combined high alkalinity, high level of sequestrant and high temperature stability of a detergent emulsion including a nonionic surfactant cannot always be achieved in the emulsion.

In accordance with the invention disclosed in applicants, co-pending United States application, Serial Number 537,567 filed June 14, 1990, it is desired to have a dishwasher composition having all of the above properties so that the dishwasher detergent liquid may be dispensed within the dishwasher by way of a dispenser which is mounted inside the dishwasher. Hence the emulsion has to be stable at the high operating temperatures of institutional type dishwashers which may be in the range of 35° to 85°C.

According to an aspect of the invention, a liquid dishwasher detergent emulsion having high alkalinity, high levels of sequestrant and high temperature stability comprises:

i) 4 to 25% w/w of an alcali metal hydroxide suitable for use in a dishwasher;

ii) 0.2 to 5% w/w of a low foaming free nonionic surfactant;

iii) 0.5 to 3% w/w of a polyacrylic acid suitable for enhancing sheeting action on non-porous surfaces;

iv) 15 to 30% w/w of a potassium polyphosphate sequestering composition enriched in tripolyphosphate and comprising minimal amounts of ortho and long-chain forms of polyphosphates to facilitate thereby solubility of said potassium polyphosphate in water;
According to another aspect of the invention, a method of formulating a liquid dishwasher detergent emulsion to provide a detergent having high alkalinity, high levels of sequestering agent and high temperature stability, said method comprising the following steps wherein each step concentrations are based on % w/w of said formulated emulsion:

i) mixing together 2 to 6% w/w of the following to form a mixture of (a) an aqueous solution of a polymeric emulsion stabilizer for said free nonionic surfactant wherein said stabilizer is a chemically associated polycarboxylic acid polymer and a nonionic surfactant formed by polymerization of said nonionic surfactant with a polymerizable reactant selected from the group consisting of acrylic acid, polyacrylic acid, copolymers of acrylic acid and an ethylenically unsaturated polycarboxylic acid or an anhydride thereof, copolymers of ethylenically unsaturated polycarboxylic acid or anhydride thereof with a non-carboxy containing ethylenically unsaturated monomer, said nonionic surfactant and said reactant being polymerized in an aqueous medium; and (b) an aqueous solution of 0.5 to 3% w/w of a polyacrylic acid suitable for enhancing sheeting action on non-porous surfaces;

ii) adjusting pH of said mixture to within the range of 8.5 to 9.5 by adding 4 to 25% w/w of an alkali metal hydroxide suitable for use in a dishwasher;

iii) adding to said mixture of step ii) with adequate stirring, 0.2 to 5% w/w of active nonionic surfactant;

iv) cooling said mixture of step ii) or iii) before, after or during addition of said nonionic surfactant to a temperature below cloud point temperature of said mixture when it includes said free nonionic surfactant;

v) mixing together the following to form a second mixture: (a) 15 to 30% w/w of active potassium polyphosphate sequestering composition enriched in tripolyphosphate and comprising minimal amounts of ortho and long-chain forms of polyphosphates to facilitate thereby solubility of said potassium polyphosphate in water; and (b) remaining alkali metal hydroxide;

vi) forming said emulsion by mixing said mixture of step iv) with said mixture of step vi).

It is generally recognized that superior cleaning of tableware, which includes dishes, flatware, glasses, cups, mugs and the like, can be achieved by dishwasher machines. The principal reason for the advantage that the dishwasher machine has over hand washing is that considerably stronger detergents and more effective rinse aids may be used in the dishwasher. Dishwashers can operate at considerably higher wash water temperatures and water rinse temperatures to achieve effective cleaning of the tableware within a one or two minute cycle. Normally, highly alkaline dishwasher detergents are used to obtain meaningful cleaning and rinsing. However, highly alkaline detergents are normally in powder form for the reasons already discussed: The formulation, according to this invention, provides however a liquid detergent emulsion which can be readily dispensed by a suitable dispenser to provide for a controlled release for each dishwasher cycle of the necessary amount of dishwasher detergent emulsion. A suitable dispenser for this type of emulsion is that defined in the aforementioned applicants, co-pending application S.N. 537,567.

It is generally understood that detergent emulsions including particularly nonionic surfactants are unstable, especially when any attempt is made to provide in combination a high alkalinity, high sequestering detergent emulsion which can withstand high temperatures. The dispenser, as identified in applicants, co-pending application, is mounted within the dishwasher. The emulsion contained in the dispenser must retain its integrity during the time it is in the container of the dispenser to ensure dispensing of a consistent concentration of emulsion components for each cycle of the dishwasher. Applicants have discovered that by a judicious selection of components for the detergent emulsion a stable emulsion system is provided which meets the demands of high alkalinity and high sequestering properties. Accordingly, the emulsion of this invention provides the combined functions of detergent action and rinse agent action to deliver the necessary performance in a variety of dishwasher machines, particularly dishwasher machines which are used in small service organizations which cannot justify large electronically controlled systems. Another significant advantage of the emulsion formulation of this invention is that it is able to accommodate a range in water hardness from soft water to very hard water by virtue of the inclusion of high levels of sequestering agent. At a 0.2% use concentration, the composition is capable of sequestering up to 175 ppm of CaCO₃. This is important in the area of "low end" dishwashers sys-
tem as used in small enterprises where it is not commercially effective to control hardness of the water supply.

It has been discovered by the applicants that the emulsion system of this invention is capable of incorporating the desired high levels of alkalinity and sequestering agent by use of a polymeric emulsion stabilizer for the free nonionic surfactant in the system and a potassium polyphosphate comprising minimal amounts of ortho and long-chain forms of polyphosphates to facilitate thereby solubility of the potassium polyphosphate in water.

By use of these two components, the necessary amounts of alkali metal hydroxide, low foaming free nonionic surfactant, polyacrylic acid sheeting agents and as needed additional sequestering agents can be incorporated into a liquid dishwasher detergent emulsion having stability even at high temperatures which would be experienced within a dishwasher.

The following discussion of the formulation of this invention provides concentrations of the various components. The concentration ranges are based on percent weight of the component per weight of the final dishwasher detergent emulsion. It is understood that where concentration percentages are provided for the components, they are based on the amount of active material unless stated otherwise.

To accomplish the high levels of alkalinity in the dishwasher detergent emulsion, anywhere from 4 to 25% w/w of an alkali metal hydroxide suitable for use in a dishwasher is provided. According to a preferred aspect of the invention, the alkali metal hydroxide may be selected from the group consisting of sodium hydroxide, and potassium hydroxide and mixtures thereof. The especially preferred hydroxide is potassium hydroxide. Within the stated broad range for the hydroxide, the preferred concentration of the hydroxide is in the range of 4 to 20% w/w.

To enhance the detergency of the composition, a defoaming free nonionic surfactant is used in the composition. The term "free" as used herein distinguishes the nonionic surfactant component of the composition from the nonionic surfactant which is incorporated in the polymeric emulsion stabilizer defined in more detail hereinafter. The concentration range for the surfactant is from 0.5 to 5% w/w with a preferred range of 0.5 to 2% w/w. It is readily appreciated that a variety of nonionic surfactants are suitable for use in dishwashers. Such surfactants may be selected from the group consisting of linear alcohol ethoxylates, block copolymers of ethylene oxide and propylene oxide, alkaline oxide adducts of polyhydric compounds, alkyl aryl oxalates and amine polyglycol condensates. Preferred nonionic surfactants may be linear alcohol ethoxylates or block copolymers of ethylene oxide and propylene oxide. A preferred ethoxylate is that manufactured and sold by BASF under the trademark PLURAFAC LF403. This ethoxylate is a liquid in its concentrated form with a cloud point of 40°C. Its pH at 5% concentration in water is 7 with a density at 23°C of 0.94.

Another preferred form of nonionic surfactant is that sold under the trademark INDUSTROL N-3 by BASF. The surfactant is an ethylene oxide and propylene oxide block copolymer with a cloud point of 28 to 33°C, an HLB value of 4.3 to 4.4 and a pH in a 2.5% solution of 5.5 ; 0.7. An example of an amine polyglycol condensate is the product Triton CF-32 (trade-mark) sold by Rohm and Haas. The material is 95% active with a Brookfield viscosity of 550 cps at 25°C. Its cloud point for a 1% solution is in the range of 20-27°C.

As is understood by those skilled in the art, polyacrylic acids are useful in dishwasher detergents to enhance sheeting action on non-porous surfaces, such as tableware. The range of the polyacrylic acid is from 0.5 to 3% w/w with a preferred concentration range of 0.5 to 1.5% w/w. There are a variety of polyacrylic acids suitable for use in dishwasher detergents. Such polyacrylic acids have a molecular weight in the range of 2000 to 4500 with a preferred molecular weight of about 4500. Preferred polyacrylic acids for use in this detergent composition are available from Rohm and Haas under the trademark ACUSOL. Two preferred ACUSOL compositions are ACUSOL 420 and ACUSOL 445. ACUSOL 420 has an average molecular weight of 2000 with partial sodium salt and 20% neutralized. The concentrate has a specific gravity at 25°C of 1.104 and a pH of 3.8 as a concentrate. Total solids in the commercially available composition is 54% with a Brookfield viscosity at 25°C of 725 ± 100 cps. The ACUSOL 445 has an average molecular weight of 4500 with partial sodium salt and 20% neutralized. The concentrate has total solids of 48% with a density of 9.2 pounds per gallon at 25°C. The pH of the concentrate is 4 and a Brookfield viscosity at 25°C of 800 cps.

In view of the emulsion being used in environments where the water hardness cannot be controlled or it is not commercially feasible to control water hardness, it is desirable to have high levels of polyphosphate sequestant in the emulsion. To ensure a stable emulsion, it has been found that a potassium polyphosphate is preferred which is enriched in tripolyphosphate. The potassium polyphosphate comprises minimal amounts of ortho and long-chain forms of polyphosphate. This feature facilitates solubility of the potassium polyphosphate in water and hence in the emulsion system. In addition, the majority of tripolyphosphate considerably enhances the cleaning performance of the composition. A preferred potassium polyphosphate is available from FMC under the trademark RAPISOL. The polyphosphate is in granular form having a P2O5 % by weight of 47.

The granular composition has very low levels of ortho-phosphate of 0 to 4% with little if any of the long chain forms of polyphosphates which are insoluble and should be removed before formulation or after the formation of the emulsion. As is appreciated, these long chain forms of polyphosphates are insoluble and thereby affect
the emulsions long term stability and forms a sediment in the parfcat. Removal of the long chain form may be accomplished by filtration with before or after formation or by centrifugation before formulation. The pH of the polyphosphate composition as a 1% solution is in the range of 9 to 9.6. The solubility of the polyphosphate in grams per kilogram of water is:

- at 10°C - 2780
- at 25°C - 1930
- at 50°C - 2160

The polyphosphate has a density in grams per cc ranging from 0.6 to 0.9.

The concentration of the potassium polyphosphate in the emulsion is very high and may range from 15 to 30% w/w. The preferred concentration of the potassium polyphosphate in the emulsion is in the range of 15 to 25% w/w. As is appreciated by those skilled in the art in building a detergent composition, there is a balance in the respective amounts of alkali metal hydroxide and polyphosphate used in the composition. This balance is generally in the form of the greater the concentration of the polyphosphate, the lower the concentration of the alkali metal hydroxide. For example, for an upper limit of the polyphosphate, the lower limit of the metal hydroxide is used and vice-versa.

In order to stabilize the emulsion of the nonionic surfactant in the system, a suitable polymeric emulsion stabilizer is employed. According to a preferred aspect of the invention, a useful polymeric emulsion stabilizer is defined in applicant's issued United States patent 4,826,618 dated May 2, 1989. The emulsion stabilizer is suitable for stabilizing the free nonionic surfactant in the liquid composition. The stabilizer is a polyacrylic acid polymeric backbone chemically associated with a nonionic surfactant. The polymeric backbone is selected from the group consisting of polyacrylic acid, copolymer of acrylic acid and an ethylenically unsaturated polycarboxylic acid or anhydride thereof, copolymers of ethylenically unsaturated polycarboxylic acid or anhydride thereof with a non-carboxylic containing ethylenically unsaturated monomer. The stabilizer may be the reaction product of acrylic acid, polycarboxylic acid and mixtures thereof polymerized in the presence of a water soluble nonionic surfactant. The concentration of the polymeric emulsion stabilizer in the composition is in the range of 2 to 6% w/w with a preferred concentration in the range of 4 to 5% w/w.

Preferred polymeric emulsion stabilizer is composed of acrylic acid groups polymerized in a head to tail manner with one or more branch points along the polymer chain. Some of the branch points consist of acrylic acid chains while the other branch points consist of linear alcohol ethoxylate or nonylphenol ethoxylate attached to the backbone by a carbon-carbon bond near the hydroxyl end of the surfactant.

Preferred polymeric emulsion stabilizers are available from Diversey Corp. and identified by terms B-35 and B-36. The B-35 stabilizer is distinguished from the B-36 stabilizer on the basis of the surfactant used in the polymerization step. In the B-35 stabilizer, the linear alcohol ethoxylate is incorporated into the chain whereas in the B-36 stabilizer, the nonylphenol ethoxylate is incorporated into the chain.

The polymeric emulsion stabilizers may be made in accordance with the details of the process provided in applicant's United States patent 4,826,618 and co-pending U.S. application S.N. 078,893 filed July 29, 1987, the disclosures of which are incorporated herein by reference. For convenience, however, a brief outline of the process is as follows.

The polymeric emulsion stabilizer employed in the present invention is produced by admixing a reactant compound selected from the group consisting of unsaturated acrylic acids, polycarboxylic acids and mixture thereof in water at concentrations between about 5 percent by weight and about 40 percent by weight based on the total weight of the solution.

The reactant compound is, generally, selected from the group consisting of acrylic acid, polyacrylic acid, copolymers of maleic anhydride and methylvinyl ether, copolymers of maleic anhydride and ethylene, copolymers of maleic anhydride and styrene, copolymers of acrylic and maleic anhydride, and mixtures thereof. Preferably, the reactant compound is selected from the group consisting of acrylic acid, polyacrylic acid and mixtures thereof. Where polyacrylic acid is employed it generally has a molecular weight below about 500,000. The polyacrylic acid generally has a molecular weight below about 40,000 to about 200,000; preferably below 50,000. Suitable polyacrylic acids are commercially available from B.F. Goodrich under the trade name GOODRITE K-722.

Also admixed in the solution is a nonionic surfactant present in an amount between about 0.4 and about 45 percent, by weight. The amount of nonionic surfactant added to the solution and adapted to be chemically associated with the polycarboxylate polymer to be formed can vary. The nonionic surfactant adapted to be bound preferably is selected from the group consisting of alcohol ethoxylates, alkyl aryl ethoxylates, products of the condensation reaction of ethylene oxide and propylene oxide, and ethylenediaminetetraacetate, adducts of ethylene oxide and propylene oxide, ethoxylated-propoxylated phosphate esters, alkylation oxide adducts of polyhydric compounds and mixtures thereof. Preferably, the surfactant employed is an alcohol ethoxylate or an alkyl aryl ethoxylate and mixtures thereof. An example of one class of compounds which can be employed...
successfully in the preparation of the modified polymeric emulsion stabilizer is the nonylphenol ethoxylates.

The nonionic surfactant chosen for preparation of this polymeric emulsion stabilizer generally has a cloud point between about room temperature and about 212°F (about 25°C to about 100°C); preferably between about 180°F and about 200°F (about 82°C and about 93°C). In general, where surfactants having cloud points in the higher portion of the preferred range are employed, higher temperatures and increased surfactant concentrations can be employed effectively. Where surfactants having lower cloud point values are employed, lower reaction temperatures and decreased surfactant concentrations can be used.

Initiation of polymerization may occur by a variety of methods. Generally, a chemical compound is added to the solution as an initiating agent. The amount of chemical initiator used in polymerization is related to the molecular mass of the polymer to be generated. The polymeric emulsion stabilizers, employed in the detergent emulsion of the present invention, preferably, have molecular mass between about 5000 and about 200,000. To obtain a polymer having a molecular mass in this range initiator, in an amount between about 0.1 and about 2.5 percent by weight based on the total solution concentration can be used.

The chemical initiator used is selected from the group consisting of alkali metal persulfates, ammonium persulfate, azobis-(isobutyronitrile), t-butyl hydro-peroxide and mixtures thereof. Such initiators are commonly referred to as oxidizing agents. Coupled initiators may also be successfully employed in the production of the polymeric emulsion stabilizer. Suitable coupled initiator include one of the above-mentioned oxidizing agents coupled with a reducing agent selected from the group consisting of hydrogen peroxide, alkali metal bisulfites, and mixtures thereof. Preferably, the reducing agent is selected from the group consisting of sodium bisulfite, hydrogen peroxide, and mixtures thereof.

The polymerization reaction preferably occurs in acidic aqueous media having a pH between about 2 and about 6. To achieve and maintain the pH at the desired level, alkali metal hydroxides may be added to partially neutralize the carboxylic acid present in solution. Such agents are preferably selected from the group consisting of alkali metal hydroxides and mixtures thereof. In the preferred embodiment, sodium hydroxide is employed.

Polymerization generally occurs at a reaction temperature between about 100°F and about 190°F over a period of between about 30 minutes and 24 hours. The polymer produced is water soluble and is present in an aqueous solution and is capable of stabilizing emulsions containing nonionic surfactants. Without being bound to any theory, it is believed that the polymer produced has a polycarboxylate backbone with approximately 1 to 5 percent by weight nonionic surfactant associated chemically therewith. The polymeric emulsion stabilizer is, preferably, maintained in an aqueous medium at a concentration between about 1 and about 40 percent by weight polymer and is employed herein as the aqueous form thereof.

The hard water sequestering properties of the potassium polyphosphate may be enhanced by use of additional sequestering agents which may be optionally provided in the composition. Concentrations of the sequestering agents when used may be up to 15% w/w with a preferred concentration in the range of up to 10 to 13% w/w. Suitable sequestering agents, which enhance the sequestering properties of the polyphosphate, include trisodium nitritolriacetate and tetratsodium methylenediaminetetraacetic acid dihydrate. The trisodium nitritolriacetate (NTA Nas) is available from several sources which include BASF, W.R. Grace & Co. (Organics Chemical Division) and Monsanto Canada Inc. The percent actives in the commercially available composition is a minimum of 40% of NTANa3 with a chelating activity in the range of 156 mg CaCO3 per gram. The pH of a 1% solution of the NTANa3 is 11 to 12.

The tetra sodium ethylenediaminetetra acetate dihydrate (EDTA) is commercially available from Clough Chemical Company Limited under the trademark QUESTAL Special. The percent actives in the commercial composition is in the range of 41% with a specific gravity of 1.32. The pH of the 1% solution is in the range of 11.6 with a cv of 12.7.

Water, as used in the aqueous solutions of the composition and as added during formulation, is preferably softened water to avoid depletion of sequestering agents. By softened water, it is intended to cover water that has minimal calcium and magnesium ions. If desired, it is appreciated that de-ionized water may be used instead of softened water for the formulation.

To achieve optimum stability for the liquid dishwasher detergent emulsion of this invention, the order in which the components of the detergent are combined is significant. It has been found by experimentation that the emulsion stabilizer in combination with the polyacrylic acid should be neutralized to a pH in the range of 8.5 to 9.5 before the addition of the nonionic surfactant. Although the need to adjust the pH is not fully understood and not wishing to be bound to the following, it is theorized that the addition of the alkali metal hydroxide causes ionization of the carboxylic groups of the emulsion stabilizer as well as the polyacrylic acid. Hence the polymeric emulsion stabilizer becomes a polyelectrolyte, where negative charges on adjacent carboxylic groups repel one another which leads to a stretching of the molecule. This stretched polymer molecule in conjunction with the added nonionic surfactant forms a mixed micelle. Should the pH be increased to a level greatly in excess of 9.5, the higher alkalinity attacks the nonionic surfactant as a competitive reaction to the micelle.
formation. Although in theory this is thought to be an explanation for the stability achieved, it has been determined through experimentation that neutralization of the acidic stabilizer and polyacrylic acid to a pH in the range of 8.5 to 9.5 significantly enhances the stability of the subsequently formed emulsion.

A second aspect in forming the emulsion is the order in which the prepared mixtures of emulsion stabilizer, polyacrylic acid, nonionic surfactant and the second mixture of potassium polyphosphate, remaining alkali metal hydroxide and sequestering agent is present. The second mixture is considerably larger in volume to form the preferred droplet size and thereby make a stable emulsion. It has been found that the first mixture is added to the second mixture with adequate stirring or agitation to form the stable emulsion.

A third aspect of the process which greatly enhances the formation of a stable emulsion is cooling of the first mixture to below the cloud point of the mixture when it includes the nonionic surfactant. As is appreciated, the cloud point of the first mixture will vary in accordance with the nonionic surfactant used and its concentration in the first mixture. For preferred components of the first mixture, it has been found that the cloud point is in the range of 9 to 14°C at a pH in the range of 9.0 to 9.5. Cooling of the second mixture is optional before combining the first mixture with the second mixture in forming the emulsion. Absence of cooling of the first mixture results in a poor emulsion which does not have sufficient stability for long term storage and use particularly at the high operating temperatures of a dishwasher.

The preferred method of formulating the liquid dishwasher detergent emulsion of this invention to provide an emulsion having high alkalinity and high levels of sequestering agent which is stable at high temperatures is as follows:

1. an aqueous solution of the polymeric emulsion stabilizer of the selected type and at an active concentration of 2 to 6% w/w is mixed with an aqueous solution of the desired polyacrylic acid solution.
2. this acidic mixture is neutralized to a pH in the range of 8.5 to 9.5 preferably 9 using a suitable alkali metal hydroxide.
3. the mixture is then cooled to a temperature below the cloud point of the mixture when it includes the free nonionic surfactant.
4. to this cooled mixture the free nonionic surfactant is then added. It is appreciated, however, that cooling may be affected alternatively after the nonionic surfactant is added to the neutralized composition or during the addition of the nonionic surfactant. This constitutes the first mixture.
5. a second mixture is formed by mixing the potassium polyphosphate with the remaining alkali metal hydroxide, preferably potassium hydroxide with a suitable sequestering enhancing agent if used. The potassium polyphosphate is optionally filtered to remove any insoluble long chain polyphosphates before inclusion in the mixture.
6. due to the heat of reaction in adding the remaining potassium hydroxide to the potassium polyphosphate, the second mixture is optionally cooled to maintain approximately room temperature. This constitutes the second mixture which is of a volume greater than the first mixture.
7. to form the emulsion, the second mixture is agitated at a sufficient rate to form an emulsion as the first mixture is added to the second mixture.
8. after complete addition of the first mixture, the resultant formulation is agitated for the desired length of time to form the stable emulsion. For example, by use of a suitable blade mixer, stirring for approximately 15 to 20 minutes after completion of addition of the first mixture to the second mixture forms a suitable stable emulsion.
9. optionally the emulsion is filtered to remove any insoluble long chain polyphosphates before the emulsion is packaged.

The following examples set out various formulations for a variety of applications to demonstrate the range of components of the formulated emulsion.

EXAMPLE 1

In accordance With the following formulation method, the compositions of Table 1 are formulated in accordance with the following method.

1. Mix water/emulsion stabilizer/polyacrylic acid.
2. Stir between each addition.
3. Neutralize to pH 9 using KOH, 45% solution.
4. Cool mixture to below 12°C.
5. Add to mixture in (4) nonionic surfactant.
6. In a separate vessel, mix RAPISOL, 60% (filtered)/QUESTAL Special/KOH, 45%.
7. Cool mixture from (6) to below 12°C.
8. With vigorous stirring (370 rpm, blade mixer) add mixture from (5) to mixture from (6).
9. Cooling can be removed.
10. Continue stirring approximately 15 to 20 minutes.

All of the formulations of Table 1 were stable. The stability tests were conducted on each of the formulations as follows. The test consisted of Freeze-Thaw Stability, Elevated Temperature Stability and Actual Use Temperature Cycling Stability.

Freeze Thaw Stability

Each product was subjected to 3 cycles of 16 hours (overnight) at -20°C with 8 hours (day) at room temperature. Quality of product was then checked.

Elevated Temperature Stability

Each product was subjected to storage at 40°C for a maximum of 3 months or until failure. Failure is considered any dramatic changes in color, viscosity or the homogeneity of the product.

Actual Use Temperature Cycling Stability

To determine a product’s stability, it is best to attempt to simulate the environments to which the products of these examples will be exposed. The formulations of Example 1 and the following Examples were placed in a Hobart AM12 machine. The formulations were in 100 ml jars. The machine was then put through 45 complete wash cycles. There was a half hour rest time between every 5 cycles of the total 45 cycles. The product was then allowed to cool after the 45 cycles were completed and the stability of emulsion evaluated.

In each of the above tests for the formulations, one consideration for a stable emulsion is that it demonstrate homogeneity after the test. As set out in the Temperature Stability tests, failure for any of the tests was considered to be any dramatic changes in color, viscosity or the homogeneity of the product.

| TABLE 1 |
|------------------|---|---|---|---|---|---|
| Formulations   | A  | B  | C  | D  | E  | F  |
| Water          | 44 | 39 | 34 | 29 | 24 | 20 |
| B35 stabilizer | 4  | 4  | 4  | 4  | 4  | 4  |
| Plurafac LF403 | 1  | 1  | 1  | 1  | 1  | 1  |
| Rapisol, 60% (filtered) | 36 | 36 | 36 | 36 | 36 | 36 |
| KOH, 45%      | 11 | 11 | 11 | 11 | 11 | 11 |
| NTA-150       | 0  | 5  | 10 | 15 | 20 | 24 |
| Acrysol LMW45X| 4  | 4  | 4  | 4  | 4  | 4  |

| TABLE 2 |
|------------------|---|---|---|---|---|---|---|---|---|
| Formulations   | A  | B  | C  | D  | E  | F  | G  | H |
| Water          | 22 | 23 | 22 | 21 | 20 | 20.8 | 31 | 22 |
| B35 stabilizer | 5  | 4  | 4  | 4  | 4  | 4  | 32 | 4  |
| Acrysol LMW45X | 2  | 2  | 3  | 4  | 4  | 4  | 4  | 2  |
| Plurafac LF403 | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  |
| Rapisol, 60% (filtered) | 36 | 36 | 36 | 36 | 36 | 36 | 36 |
| KOH, 45%      | 10 | 10 | 10 | 10 | 10 | 11 | 10 | 11 |
| NTA-150 (4.5%) | 24 | 24 | 24 | 24 | 24 | 24 | 24 | 24 |
EXAMPLE 3

In accordance with the formulation method and stability test of Example 1, the compositions of Table 3 were made to form stable emulsions.

<table>
<thead>
<tr>
<th>Formulations</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
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<td>Water</td>
<td>11</td>
<td>7</td>
<td>11.2</td>
<td>7</td>
<td>16</td>
<td>10.2</td>
<td>9.2</td>
<td>13</td>
</tr>
<tr>
<td>B35 stabilizer</td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>0</td>
<td>5</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Acrysol LMW45X</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Industrol N-3</td>
<td>1</td>
<td>0.8</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Rapisol, 60% (filtered)</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>37</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>KOH, 45%</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Questal Special (42.8%)</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>36</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>33</td>
</tr>
</tbody>
</table>

EXAMPLE 4

In accordance with the formulation method and stability test of Example 1, the compositions of Table 4 were made to form stable emulsions.

<table>
<thead>
<tr>
<th>Formulations</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>4</td>
<td>92</td>
<td>8.2</td>
<td>7.2</td>
<td>11</td>
</tr>
<tr>
<td>B35 stabilizer</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Acrysol LMW45X</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Industrol N-3</td>
<td>1</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>Rapisol, 60% (filtered)</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>KOH, 45%</td>
<td>46</td>
<td>46</td>
<td>46</td>
<td>46</td>
<td></td>
</tr>
</tbody>
</table>

EXAMPLE 5

In accordance with the formulation method and stability test of Example 1, the compositions of Table 5 were made to form stable emulsions.

<table>
<thead>
<tr>
<th>Formulations</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>11</td>
<td>12</td>
<td>10.2</td>
<td>9.2</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>B35 stabilizer</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Acrysol LMW45X</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Plurafac LF403</td>
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<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Rapisol, 60% (filtered)</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>37</td>
<td>36</td>
</tr>
<tr>
<td>KOH, 45%</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Questal Special</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>36</td>
<td>36</td>
</tr>
</tbody>
</table>

EXAMPLE 6

In accordance with the formulation method and stability test of Example 1, the compositions of Table 6 were made to form stable emulsions.
Claims

1. A liquid dishwasher detergent emulsion having high alkalinity, high levels of sequestrant and high temperature stability, said detergent emulsion comprising:
   i) 4 to 25% w/w of an alkali metal hydroxide suitable for use in a dishwasher;
   ii) 0.2 to 5% w/w of a low foaming free non-ionic surfactant;
   iii) 0.5 to 3% w/w of a polyacrylic acid suitable for enhancing sheeting action on non-porous surfaces;
   iv) 15 to 30% w/w of a potassium polyphosphate sequestering composition enriched in tripolyphosphate and comprising minimal amounts of ortho and long forms of polyphosphates to facilitate thereby solubility of said potassium polyphosphate in water;
   v) 2 to 6% w/w of a polymeric emulsion stabilizer for said free nonionic surfactant, the polymeric emulsion stabilizer being a chemically associated polycarboxylic acid polymer and a nonionic surfactant formed by polymerization of said nonionic surfactant with a polymerizable reactant selected from the group consisting of acrylic acid, polyacrylic acid, copolymers of acrylic acid and an ethylenically unsaturated polycarboxylic acid or an anhydride thereof, copolymers of ethylenically unsaturated polycarboxylic acid or anhydride thereof with a non-carboxy containing ethylenically unsaturated monomer, said nonionic surfactant and said reactant being polymerized in an aqueous media;
   vi) 0 to 15% w/w of a sequestering agent to enhance hard water sequestering characteristics of said potassium polyphosphate; and
   vii) water to make up the balance of composition to 100% w/w.

2. A liquid dishwasher detergent emulsion of claim 1, wherein said alkali metal hydroxide is potassium hydroxide.

3. A liquid dishwasher detergent emulsion of claim 1 or 2, wherein said selected nonionic surfactant is said linear alcohol ethoxylate.

4. A liquid dishwasher detergent emulsion of claim 1 or 2, wherein said selected non-ionic surfactant is said block copolymer of ethylene oxide and propylene oxide.

5. A liquid dishwasher detergent emulsion of claim 1, 2, 3 or 4 wherein said potassium polyphosphate has a solubility in water at 250°C in range of 1900 gm/l.

6. A liquid dishwasher detergent emulsion of claim 1, 2, 3, 4, or 5 wherein said emulsion stabilizer is selected from the group consisting of acryic acid groups polymerized with linear alcohol ethoxylate.

7. A method of formulating a liquid dishwasher detergent emulsion to provide a detergent having high alkalinity, high levels of sequestrant and high temperature stability, said method comprising the following steps wherein each step concentrations are based on % w/w of said formulated emulsion:
   i) mixing together 2 to 6% w/w of the following to form a mixture of (a) an aqueous solution of a polymeric emulsion stabilizer for said free nonionic surfactant wherein said stabilizer is a chemically associated polycarboxylic acid polymer and a nonionic surfactant formed by polymerization of said nonionic surfactant with a polymerizable reactant selected from the group consisting of acrylic acid, polyacrylic acid, copolymers of acrylic acid and an ethylenically unsaturated polycarboxylic acid or an anhydride thereof, copolymers of ethylenically unsaturated polycarboxylic acid or anhydride thereof with a non-carboxy...
containing ethylenically unsaturated monomer, said nonionic surfactant and said reactant being polymerized in an aqueous media; and (b) an aqueous solution of 0.5 to 3% w/w of a polyacrylic acid suitable for enhancing sheeting action on non-porous surfaces;

ii) adjusting pH of said mixture to within the range of 8.5 to 9.5 by adding 4 to 25% w/w of an alkali metal hydroxide suitable for use in a dishwasher;

iii) adding to said mixture of step ii) with adequate stirring, 0.5 to 5% w/w of active non-ionic surfactant;

iv) cooling said mixture of step ii) before, after or during addition of said non-ionic surfactant to a temperature below cloud point temperature of said free non-ionic surfactant;

v) mixing together the following to form a second mixture: (a) 15 to 30% w/w of active potassium polyphosphate sequestering composition enriched in tripolyphosphate and comprising minimal amounts of ortho and long forms of polyphosphates to facilitate thereby solubility of said potassium polyphosphate in water; and (b) remaining alkali metal,

vi) cooling said mixture of step v) to a temperature below cloud point temperature of said free non-ionic surfactant;

vii) forming said emulsion by mixing said mixture of step iv) with said mixture of step vi).

8. A method of claim 7, wherein vigorous stirring is applied to said mixture of step vii) to form said emulsion.

9. A method of claim 7, wherein step v), up to 15% w/w of a sequestering agent to enhance hard water sequestering characteristics of said potassium polyphosphate is mixed into said second mixture.

10. A method of claim 7, wherein said step iv) cooling said mixture of step ii) before, during or addition of said nonionic surfactant.