

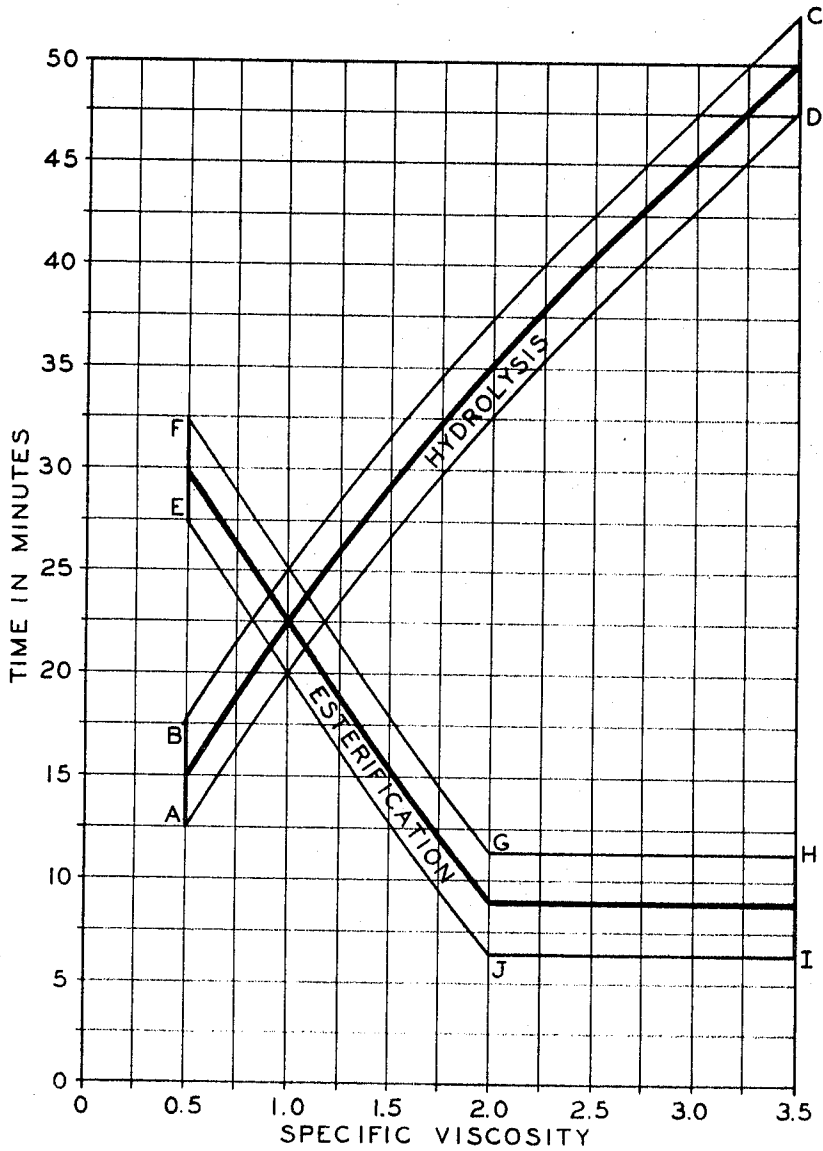
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LIQUID DETERGENT PROCESSES

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LIQUID DETERGENT PROCESSES

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ABSTRACT OF THE DISCLOSURE

A process for manufacturing a liquid detergent composition comprising the steps of (a) partially hydrolyzing a copolymer of vinylmethyl ether and maleic anhydride at specific temperatures and for specific periods of time, (b) intermixing the partially hydrolyzed material with a synthetic organic detergent active material containing at least one hydroxyl radical, (c) esterifying the polymer by maintaining certain temperatures and pH ranges for a specific period of time and (d) thereafter raising the pH of the detergent material to at least about 9.

The present invention relates to processes for manufacturing liquid detergent compositions. More particularly, the present invention relates to processes for manufacturing liquid detergent emulsion compositions that exhibit excellent stability against phase separation even though they contain relatively high concentrations of dissolved inorganic salts and of synthetic organic detergent components.

The many benefits which can result from the utilization of effective detergent compositions that are liquid in form are widely appreciated. In order to be competitive with the well-known "dry" powdered or granulated detergents, liquid detergent compositions must contain high concentrations of both inorganic "builder" salts; for example, phosphates, silicates, carbonates and sulfates, (usually dissolved in water); and organic detergent active materials. Because of the presence of high-concentrations of inorganic salts in water, very little, if any, of the organic detergent active material can actually be dissolved in water. Therefore, if a detergent manufacturer wishes to make a reasonably competitive liquid detergent, he must ordinarily either disperse or emulsify the detergent active material into the concentrated salt solution.

While the emulsification or dispersion per se of most detergent active materials in concentrated salt solutions is not difficult, it has heretofore been very difficult to manufacture liquid detergents containing such dispersed detergent active materials that are stable for an extended period of time against separation of the detergent active material from the concentrated salt portion of the detergent composition (i.e., stable against phase separation). Since consumers of liquid detergents generally feel that liquid detergents which "separate" are objectionable, it can readily be appreciated that manufacturers of concentrated liquid detergents have as one of their foremost objectives the production of liquid products that are stable against phase separation for as long a time as possible under any or all of the usual warehousing, shipping and storage conditions to which the liquid detergent compositions are exposed.

Because of the impracticability of testing thousands of detergent formulations under various end-use conditions in order to determine whether or not a given formulation is of acceptable stability, a test was devised to stimulate prolonged storage conditions. The results of this test were subsequently found to correlate well with data from actual prolonged storage of the liquid detergent formulations tested. Briefly, the test involves centrifugation of the material (at about 30° C.) under approximately 1000

gravities for 60 minutes in a calibrated glass centrifuge tube. Formulations that exhibit less than 6% (by volume) visible "separation" in this very extreme test are considered acceptable (and will exhibit excellent stability against phase separation under normal storage and handling conditions), while those that exhibit more than 6% "separation" are not acceptable. This test will be described in greater detail in Example I, below.

Relatively stable emulsions can be made, of course, if extremely high viscosity emulsions (i.e., having apparent viscosities of 1500 centipoises or more) are produced. However, such "high viscosity" emulsions depend solely upon their viscosity for their stability, and are not desirable for liquid detergent emulsions because products having such very high viscosity have poor pouring draining characteristics (from containers). The liquid detergent emulsions to which the present invention is directed are those having apparent viscosities of less than 900 centipoises, as measured by a Brookfield viscometer using a number 3 spindle, at 30 r.p.m. and at 25° C., and preferably having apparent viscosities of from about 150 to about 800 centipoises.

The use of certain polymeric materials, and mixtures of certain polymeric materials, to aid in the stabilization of liquid detergent emulsion compositions has been disclosed heretofore. For example, the use of several specified polymers is described in detail in U.S. Patent No. 3,060,124. The polymers disclosed in this patent become effective stabilizers when they are simply dissolved into or dispersed well through the liquid detergent emulsion composition. The number of polymers that can act as effective stabilizers for liquid detergent emulsion compositions via simple dispersion and/or dissolution in the detergent formulation is, however, very small. In addition, whether or not a given polymer can perform as a stabilizer for liquid detergent emulsion compositions cannot presently be predicted in advance. The polymer must first be tested in an actual formulation before its value as a stabilizer can be determined.

One class of polymeric material which is both relatively inexpensive and commercially available is that known as the class of copolymers of methyl vinyl ether and maleic anhydride. Although copolymers of methyl vinyl ether and maleic anhydride have been considered heretofore for use as stabilizers for liquid detergent emulsion compositions, no procedure was known heretofore whereby detergent compositions containing commercially economical amounts of such copolymers could be stabilized sufficiently to be considered "acceptable" in the aforementioned stability test.

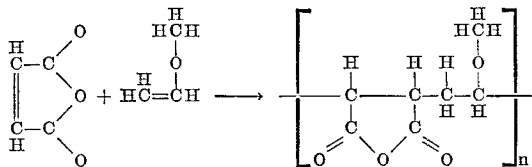
The invention claimed herein is based upon the discovery that unless critical limitations of method of processing the liquid detergent emulsion compositions are observed, the use of copolymers of methyl vinyl ether and maleic anhydride in such compositions does not result in the manufacture of commercially acceptably stable products; whereas by observing these critical limitations, products are obtained which are surprisingly stable, even under the very extreme conditions of the above-described test.

Thus, it has been discovered that unless certain critical process limitations are observed with respect to (1) hydrolysis of the copolymers of methyl vinyl ether and maleic anhydride and (2) partial esterification of the hydrolyzed copolymers; which process limitations involve time, temperature and pH of the systems involved; excellent emulsion stability cannot be obtained by use of such copolymers, whereas by following certain critical limitations (which will be detailed hereinafter), very stable liquid detergent emulsions can be obtained.

The unexpectedly high emulsion stability that results from practicing the present invention results when: (a)

certain copolymers of methyl vinyl ether and maleic anhydride are first partially hydrolyzed by treatment with water under carefully controlled conditions of temperature and pH for a certain critical period of time; (b) the resulting (partially) hydrolyzed copolymer is reacted with a surfactant (via a partial esterification reaction) containing at least one reactive hydroxyl radical in its molecule under carefully controlled, critical conditions of temperature, pH and time (while at least part of said surfactant is being maintained in an emulsified condition—dispersed in an aqueous continuous phase); and subsequently (c) bringing the pH of the resulting “partially esterified” aqueous emulsion to above about 8.5, preferably into the range of from about 9.5 to about 10.5.

The copolymers (or “interpolymers”) of vinyl methyl ether and maleic anhydride useful in the practice of this invention are those reaction products of the following reaction:



having specific viscosities (measured in the usual way by dissolving 1 part by weight of the essentially anhydrous copolymer in 99 parts by weight of dimethylformamine, and subsequently measuring the specific viscosity of the resulting solution at 25° C. by modification of ASTM method D-445-446T, method B, using an Ostwald viscometer), between about 0.5 and 3.5. The molecular weight of such copolymers may range from about 400 to more than 2 million.

The synthetic organic detergents that have been found especially useful in the practice of the present invention are those which are water soluble (i.e., soluble in water at room temperature to the extent of at least about 0.1 to 0.3 weight percent, which is about the concentration at which detergents are generally utilized to wash clothes or dishes, for example) and contain at least one hydroxyl group attached directly to a carbon atom (through an O—C bond). They can be either “nonionic” or “anionic” in nature, but of these, the nonionic synthetic organic detergents are preferred. The general class of water-soluble nonionic and anionic synthetic organic detergents (that contain at least one hydroxyl group in their molecule) is well-known by those skilled in the art and include, for example, condensation products resulting from the inter-reaction of one or more lower alkylene oxides (such as ethylene oxide, propylene oxide, butylene oxide, butylene dioxide, epichlorohydrin, isobutylene oxide, and the like) with a compound having what is termed at least one “reactive hydrogen” [such as, for example, alkylphenols including nonylphenol, dodecylphenol, octylphenol, dinonylphenol, diisopropylphenol, diamylphenol, dibutylphenol, as well as other alkylphenols wherein the alkyl group (or groups) contain a total of from about 4 to about 20 carbon atoms; alkyl cesols, wherein the alkyl group (or groups) contain a total of from about 4 to about 20 carbon atoms; alcohols containing from about 6 to about 30 carbon atoms (such as lauryl alcohol, mixed “cocoanut” alcohols, oxtotridecyl alcohol, oleyl alcohol, hydrogenated tallow alcohols, and the like); the alkyl mercaptans such as dodecylmercaptan, tridecylmercaptan, octadecylmercaptan and the like, wherein the alkyl group contains from about 8 to about 25 carbon atoms; aliphatic amides such as tridecylamide, hexadecylamide, nonylamide, and the like, wherein the amide contains from about 6 to about 30 carbon atoms; alkyl or aliphatic sulfonamides such as dodecylsulfonamide, tetradecylsulfonamide, tetradecenylsulfonamide and the like, wherein the aliphatic or alkyl radical contains from about 8 to about 24 carbon atoms; the polypropylene oxides and polybutylene oxides having

molecular weights of from about 750 to about 4000; reaction products of propylene oxide and/or butylene oxide with polyamines such as ethylenediamine, diethylene triamine, triethylenetetramine and the like, which reaction products have molecular weights of from about 750 to about 4000; products resulting from the condensation of a lower alkylolamine (such as monoethanolamine, diethanolamine, dimethylolamine, isopropanolamine, di-n-propanolamine, and the like) with a fatty acid containing from about 8 to about 24 carbon atoms], as well as many other materials.

Examples of water-soluble anionic synthetic organic detergents have the requisite hydroxyl radical in their molecule include the hydroxy-substituted fatty acids (such as alpha-hydroxy stearic acid, beta-hydroxy oleic acid, 4-hydroxy lauric acid, and the like); esters of fatty acids that contain between 8 and 24 carbon atoms (wherein the requisite hydroxyl radical can be in either the fatty acid or the “alcohol” portion of the molecule); as well as many other anionic materials.

The foregoing examples of nonionic and anionic synthetic organic detergents are by no means exhaustive of those that can be used successfully in the practice of the present invention. Thus, any surfactant (detergent) that has a hydroxyl group in its molecule and is sufficiently water soluble can be used in the practice of the present invention. Many other materials that meet these qualifications can readily be found in Schwarz and Perry's two books: “Surface Active Agents,” volumes I and II, Interscience Publishers, New York (1958 and 1959).

Minor proportions (as compared to the amount of the polyoxyalkylene detergent active materials that are utilized) of other detergent materials can be used to supplement the above-described polyoxyalkylene detergent-active materials in the practice of the present invention. Typical of these other types are the detergent active or surface active aromatic sulfonates which are free of polyoxyalkylene chains, such as the sodium sulfonate of an alkylated aromatic hydrocarbon. These sulfonates are usually prepared by alkylating an aromatic hydrocarbon of the class consisting of benzene, toluene, xylene, for example, with aliphatic or olefinic hydrocarbons having from 9 to 18 carbon atoms, and then sulfonating and neutralizing the resulting alkylaromatic hydrocarbon. Another example of detergent-active materials that can supplement the polyoxyalkylene detergent-active materials described hereinbefore are the alkylolamides having from 10 to 20 carbon atoms in the acid portion of the molecule. These alkylolamides are formed by reacting of fatty acid, such as tall oil fatty acid, coconut fatty acids, stearic acid, lauric acid, etc., with an alkylolamine such as monoethanolamine, diethanolamine, monoisopropanolamine, diisopropanolamine, mono-n-propanolamine, di-n-propanolamine, etc. Ordinarily, these “supplemental” (to the hydroxyl-containing materials) detergent active materials can be utilized in the compositions within the scope of this invention at levels of from a mere trace to several weight percent. However, the preferred liquid detergent compositions contain no more than about 60 weight percent of such supplemental materials based on the hydroxyl-containing detergent active material employed.

One can employ in the practice of this invention, a solution of any inorganic or organic water-soluble salt which it is desired for “building” or for any other reason, to incorporate into a detergent composition, so long as the salt is compatible with the other components of the composition. Well-known precautions should be observed in mixing the various materials in the practice of the invention. Ordinarily, the compatible salts that can be employed are those which are soluble in distilled water to the extent of at least about 5 weight percent. And where raw material cost considerations are important, these salts will be inorganic in nature. As a practical matter, however, because of economic considera-

tions as well as the necessity to include in the liquid detergent compositions as high a level as is practicable of materials which can sequester "hardness" ions, such as calcium, magnesium, and iron, the salts which are preferably utilized are the alkali metal chain phosphate salts (such as, for example, the alkali metal pyrophosphates such as tetrasodium pyrophosphate, tetrapotassium pyrophosphate, etc.), the acid pyrophosphates such as disodium pyrophosphate, trisodium monohydrogen pyrophosphate, dipotassium dihydrogen pyrophosphate, etc., the tripolyphosphates and acid tripolyphosphates such as sodium tripolyphosphate ($\text{Na}_3\text{P}_2\text{O}_{10}$), potassium tripolyphosphate ($\text{K}_3\text{P}_3\text{O}_{10}$), tetrasodium monohydrogen tripolyphosphate ($\text{K}_4\text{HP}_3\text{O}_{10}$), tripotassium dihydrogen tripolyphosphate ($\text{K}_3\text{H}_2\text{P}_3\text{O}_{10}$), etc., the alkali metal tetrapolyphosphates such as hexasodium and hexapotassium tetrapolyphosphate, etc., the alkali metal hexametaphosphates and higher chain length chain polyphosphates such as those that are present in the sodium, potassium, and lithium phosphate "glasses" (usually prepared by melting a mixture of phosphate salts having an $\text{M}_2\text{O}/\text{P}_2\text{O}_5$ ratio between about 1.0 and about 1.3 where M is an alkali metal, and "quenching" the resulting product to yield a mixture of chain polyphosphate salts of varying molecular weight), and the like (wherein the particularly preferred alkali metal salts are potassium and sodium). Of these, tetrapotassium pyrophosphate is most preferred. Other water-soluble sequestering agents such as alkali metal ethylene diamine, alkali metal citrate, alkali metal tartrate, etc., can also be utilized to advantage in the composition. It should be understood that while reference herein is made specifically to the alkali metal chain phosphate salts, other inorganic salts, and water-soluble sequestering agents can generally be utilized either in place of all of the phosphate salt, in place of some of it, or in addition to it.

Another ingredient which can be utilized along with the above described detergent compounds and chain-polyphosphates in the aqueous detergent solutions prepared according to this invention are the water-soluble sodium and potassium silicates. As is well-known, sodium silicates can vary quite widely in composition, ranging from tetra- and disilicates having a mol ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ of 1:4 and 1:2, respectively, to the more alkaline silicates, such as the orthosilicates having a mol ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ of 2:1. In general, potassium silicate ($\text{K}_2\text{O}:\text{SiO}_2$ -1:2.1) is the preferred compound silicate for use according to the present invention. However, other silicates, or mixtures of silicates, having overall mol ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ between about 1:1 and 1:4 may be used.

Inorganic alkali metal carbonates can also be employed. The carbonates employed are preferably the potassium carbonates such as commercial pearl ash or modified potassium carbonates having various degrees of alkalinity. Minor amounts of additional ingredients, such as borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and potassium or ammonium borates, dyes, perfumes, etc., can also be incorporated into the liquid detergent. Additionally, the ultimate concentrate mixture is preferably formulated so that an aqueous solution of about 0.25 weight percent has a pH of between about 8.5 and about 10.5.

The particular quantities of any of the aforementioned materials (other than the special surfactant that is reacted with the copolymer of vinyl methyl ether and maleic anhydride, and the copolymer itself) that are utilized in the liquid detergent emulsions that are made in accordance with the processes of the present invention are not critical: any particular material being present in a given detergent formulation in accordance with the particular end use intended for the stabilized detergent composition. However, for general purpose detergent usage, the following practice is suggested. In making up liquid detergent emulsions according to the present invention, the aforementioned ingredients can, for example, be utilized in the following proportions: (1) from about 1

to about 25, and preferably from about 3 to about 15 percent by weight of active detergent compound; (2) from about 10 to about 50, and preferably from about 15 to about 25 percent by weight of phosphate; (3) from 0% to 10%, and preferably from about 2% to about 8% of water-soluble silicate (calculated on the basis of anhydrous silicate material); all of these percentages being based upon the final liquid detergent composition.

The liquid formulations of the present invention generally contain from about 30% to about 75% and preferably from about 40% to about 65% by weight of water based upon the total liquid detergent. Alcohols, such as ethanol and glycols, such as ethylene glycol or propylene glycol may also be employed in the present detergent compositions, if necessary to improve the compatibility of the various components over a wide range of temperature conditions. The proportion of alcohol or glycol may be from 1% to 10% by weight.

The present products have been found to be of particular utility in automatic washers as a liquid concentrate, which is readily pumped through pipes and tubing into the washing chamber. These compositions may be stored for prolonged periods of time without separation into organic and inorganic layers. This is essential in the production of a liquid detergent which is to be utilized in small increments during a long period of storage.

The reasons for the unexpectedly superior stability of the liquid detergent emulsions that are prepared in accordance with the processes of this invention are not known. It is a fact, however, that when critical process limitations outlined hereinbefore are observed, exceptionally stable, valuable liquid detergent emulsions result. The present processes can be divided for the sake of clarity into three distinct steps; namely, (1) hydrolysis, (2) esterification, and (3) "pH-raising." Although in the following discussion, these various steps will be described separately, it will be understood that the overall processes of this invention can be performed in both "batch" and "continuous" types of operations.

The "hydrolysis" step of the present processes must be performed while the copolymer is dispersed through (or maintained completely in contact with the water therein in some other manner) a liquid aqueous medium having a pH below 4.5 (preferably from about 2.5 to about 4). In addition, the temperature of the acidic aqueous medium or solution must be between about 70° C. and about 105° C. (preferably between about 75° C. and about 90° C. for optimum results) for a certain critical period of time, which period of time has been found to vary somewhat depending upon the specific viscosity of the particular copolymer being employed. At temperatures below this critical range, the necessary type of hydrolysis of the copolymer apparently does not occur, or occurs so slowly as to make any process resulting from use of such low "hydrolysis" temperature impractical. The "critical period of time" referred to above can actually vary to a relatively small extent (generally within an overall range of about 5 minutes) for the particular copolymer being employed. Thus, in the figure of the drawings, any point within the area designated ABCDA which falls upon the vertical line corresponding to the specific viscosity of the particular copolymer employed represents the "critical period of time" mentioned above, while the point (on such vertical line) falling upon the heavy black line bisecting area ABCDA in the figure represents an approximately optimum time condition. Note that the above-described "hydrolysis" step apparently does not result in complete hydrolysis of the copolymer (since the use of substantially longer hydrolysis periods than those designated above—other factors being equal—results in final liquid detergent emulsions that do not have the excellent stability of those made via the processes of this invention).

The "esterification" step of the present processes involves essentially the intermixing a quantity or an amount

of a surfactant that is capable of reacting with the "hydrolyzed" groups (apparently the free carboxylic acid groups) on the partially hydrolyzed copolymer (resulting from the "hydrolysis" step described above) to form ester groups. Thus the surfactant must contain at least one free hydroxyl group. "Reactive" surfactants of this type are described in detail hereinbefore. Any amount of such "reactive" surfactant can be used during this "esterification" step within the range of from about 0.1 to about 25 weight percent, based on the total weight of the resulting "esterification" mixture (containing the partially hydrolyzed copolymer, the surfactant, and the aqueous medium); but apparently more than that amount of "reactive" surfactant necessary to saturate the aqueous medium must be present during the "esterification" step. Preferably, the amount of surfactant should be within the range of from about 0.5 to about 12 weight percent during the "esterification" step. In addition, the temperature and the pH of the aqueous medium should be closely controlled for a certain critical period of time during the "esterification" step. Thus, the temperature must be maintained within the range of from about 70° C. and about 105° C. (preferably between about 70° C. and about 95° C. for optimum results, and the pH of the aqueous medium must be below about 8 (preferably between about 3 and about 7.5) during this "critical period of time."

The "critical period of time" referred to with respect to the "esterification" step of the present processes can vary to some extent (generally within an overall range of about 5 minutes) the particular range being determined by the particular copolymer involved; generally higher molecular weight copolymers require shorter "esterification times." Thus, any point within the area designated EFGHIJE in the figure of the drawings which falls upon the vertical line corresponding to the specific viscosity of the particular copolymer employed represents such "critical period of (esterification) time," while the point (on such vertical line) falling upon the heavy black line bisecting area EFGHIJE in the figure represents an approximately optimum time condition for the given copolymer. Only partial esterification of the acidic (partially hydrolyzed) copolymer occurs during the above-described "esterification" step.

During the "hydrolysis" and "esterification" steps detailed above the pH of the aqueous medium can be maintained in any desired manner. For example, organic or inorganic acids can be present in the aqueous medium in order to help maintain the desired acidic pH during the acidic "hydrolysis" step, and even during the "esterification" step. The presence of other materials in the aqueous medium apparently has no deleterious effect on the overall desired reactions so long as the pH conditions detailed above are met (and so long as there is enough water present in each instance to maintain the aqueous medium in the liquid or "fluid" condition). Also, the "esterification" step need not be performed immediately after the "hydrolysis" step. Thus, if desired, the aqueous medium containing the partially hydrolyzed copolymer (resulting from the "hydrolysis" step) can be preserved for prolonged periods of time and temperatures significantly below about 70° C. (preferably below about 50° C.) without significantly destroying the ability of the partially hydrolyzed copolymer to react with the surfactant when it is subsequently utilized under "esterification" conditions (described above). Similarly, the "hydrolysis" and "esterification" steps can be interrupted by cooling the aqueous medium, for example, without destroying these advantageous processes, so long as the overall "hydrolysis times" and "esterification times" (in accordance with the drawings) under the critical conditions described above are ultimately observed, or at least so long as the desired extent of hydrolysis and esterification have taken place.

The name of the so-called "pH-raising" step of the

present processes implies what actually must occur in order to "finish off" the stabilized liquid detergent emulsions of this invention. During this step the pH of the aqueous medium (containing the partially esterified copolymer-surfactant mixture) is raised to at least about 8.5, thereby preventing any additional acidic hydrolysis or esterification from occurring. Apparently, it is only the raising of the pH which is critical during this step of the processes of the present invention. Any basic material that is capable of raising the pH of the aqueous medium resulting from the above-described "esterification" step to above about 8.5 when it is simply intermixed therewith can be used. Hundreds of materials having such capability are well-known to those skilled in the art, and need not be detailed here. For example, any of the above-described alkali metal polyphosphate salts that are basic in nature (have no free acidic groups) can be used. Of these, tetrapotassium pyrophosphate and potassium tri-polyphosphate are particularly preferred. By use of such basic, water-soluble polyphosphate salts to adjust the pH of the aqueous media (containing the partially esterified polymer) to above about 8.5, a double purpose is served; the resulting solution then already contains "builder" salts, if such "builder" salts are desired therein. Additional surfactant can be either dissolved or emulsified into the aqueous medium either before or during this "pH-raising" step.

In the following examples, which illustrate some of the preferred embodiments of the present invention, all parts given are by weight unless otherwise stated.

Example I

Into a conventional jacketed (for water cooling or steam heating) stainless steel mixing vessel fitted with a high speed, 6-bladed, turbine-type agitator (wherein the diameter of the turbine blades is about one-half the diameter of the mixing vessel) are poured 2990 parts of water. The water is heated to about 80° C. While mixing steadily, 80 parts of a powdered, anhydrous copolymer of vinyl methyl ether and maleic anhydride (having a specific viscosity of 0.5) are added slowly over a 2 minute period of time. In a "hydrolysis" step, the resulting mixture is then stirred at 80° C. for an additional 14 minutes in order to partially hydrolyze the copolymer.

Into the resulting acidic mixture are then added (over 1 minute of time and with very intense agitation) a mixture (preheated to about 80° C.) of 300 parts of disodium dihydrogen pyrophosphate and 1100 parts of an adduct of dodecylphenol and ethylene oxide. (The adduct was made by condensing 10 moles of ethylene oxide with one mole of dodecylphenol.) In an "esterification" step, the resulting emulsion is then continuously stirred at about 80° C. for 30 minutes. Then 4110 parts of a 60 weight percent aqueous solution of tetrapotassium pyrophosphate are added to the "partially esterified" emulsion over about 3 minutes, after which 550 parts of a 45 weight percent aqueous solution of potassium hydroxide are added. Addition of the KOH results in a slight increase in temperature to about 86° C. The resulting mix is then cooled to about 81° C., and 800 parts of a 35 weight percent aqueous solution of sodium silicate ($\text{Na}_2\text{O}/\text{SiO}_2=2.4$) are added over 2 minutes' time. The resulting mixture is then stirred for an additional 5 minutes, cooled to about 40° C., and packaged for sale to the ultimate consumers. Its pH is 10.2.

The stability of the product is then tested by subjecting 200 mls. of it in a calibrated centrifuge tube to 1000 times gravity in a conventional centrifuge for one hour. At the end of this test, only 4 volume percent of clear solution is observed at the bottom of the centrifuge tube. Thus "separation" in this test is only 4 volume percent, the product is rated "acceptable," in accordance with the foregoing discussion.

Still another test to which the product is subjected is a storage test in an oven held at 50° C. for six weeks. The

product is found to be stable in this test, also; showing no visible sign of phase separation after being stored for this period of time.

In a manner practically identical to that of Example I above, several other anhydrous copolymers of vinyl methyl ether and maleic anhydride are utilized for the manufacture of phase-stabilized liquid detergent emulsions. Data therefor is shown in table below. "Hydrolysis Time" and "Esterification Time" in table correspond to the amount of time, respectively, allotted for the hydrolysis¹ step and the "esterification" step designated as such in Example I.

TABLE I

Example	Specific ¹ viscosity	Hydrolysis time (min.)	Esterification time (min.)	Percent phase ² separation	Stability ³ at 50° C.
II.....	0.8	19	25	3	Excellent.
III.....	1.0	22.5	22.5	0	Do.
IV.....	1.2	25	21	5.5	Do.
V.....	1.4	17	28	4	Do.
VI.....	1.65	13	32	6	Do.
VII.....	1.85	10	33	4	Do.
VIII.....	2.0	8	35	4	Do.
IX.....	2.1	9	36.5	2	Do.
X.....	2.35	85	38	5	Do.
XI.....	2.65	8	42	4	Do.
XII.....	2.9	8.5	44	5.5	Do.

¹ Specific viscosity of the copolymer used.

² Volume percent.

³ Test conducted at 50° C. for 6 weeks. Excellent rating given when less than 5 volume percent of separation occurs during test.

What is claimed is:

1. A process for manufacturing a liquid detergent composition, which process comprises the steps of

(a) preparing an acidic aqueous polymer dispersion by partially hydrolyzing a copolymer of vinyl methyl ether and maleic anhydride having a molecular weight of above 400 with water; said hydrolysis being conducted at a temperature between about 70° C. and 105° C. and under acidic conditions the amount of said copolymer being from about 0.3 to about 5 weight percent of said acidic aqueous polymer dispersion;

(b) intermixing to form an emulsion with said acidic aqueous polymer dispersion an amount of a synthetic organic detergent active material containing at least one hydroxyl radical selected from the group consisting of anionic detergent active materials, nonionic detergent active materials and mixtures thereof; said amount being more than enough to saturate the resulting mixture and being from about 0.1 to about 15 weight percent, based on the total weight of said resulting mixture;

(c) converting said resulting mixture into an aqueous esterified polymer dispersion by maintaining the temperature of said resulting mixture between about 70° C. and about 105° C. and the pH of said resulting mixture below 8 until the partially hydrolyzed acidic copolymer of vinyl methyl ether and maleic anhydride has been partially esterified by reaction with said synthetic organic detergent active material; and

(d) thereafter raising the pH of the resulting emulsion composition to at least about 9;

wherein the amount of time during which steps (a) and (c) are carried out falls within the areas designated ABCDA and EFGHIJE, respectively, in FIGURE 1, depending upon the specific viscosity of said copolymer of vinyl methyl ether and maleic anhydride; said specific viscosity being from about 0.5 to about 3.5.

2. A process for manufacturing a liquid detergent

emulsion composition, which process comprises the steps of

(a) intermixing with water from about 0.3 to about 5 weight percent, based on the weight of the resulting first mixture, of a copolymer of vinyl methyl ether and maleic anhydride having a specific viscosity between about 0.5 and about 3.5 and a molecular weight above about 400, the pH of said resulting first mixture being from about 2.5 to about 4;

(b) partially hydrolyzing said copolymer to thereby form an acidic aqueous dispersion by maintaining the temperature of said resulting first mixture at from about 75° C. to about 90° C. for a first period of time;

(c) forming a liquid emulsion by intermixing with said resulting first mixture from about 0.5 to about 12 weight percent, based on the weight of said liquid emulsion, of a nonionic synthetic organic detergent containing at least one hydroxyl radical to thereby form a second mixture; the pH of said second mixture being from about 3 to about 7.5;

(d) reacting together the partially hydrolyzed copolymer in said second mixture and said nonionic synthetic organic detergent to thereby form an esterified emulsion by maintaining the temperature of said second mixture between about 70° C. and about 95° for a second period of time while said nonionic synthetic organic detergent is retained in an emulsified condition;

(e) thereafter increasing the pH of said esterified emulsion to between about 9 and about 11; and blending into said esterified emulsion from about 15 to about 30 weight percent, based on the weight of said emulsion composition, of an inorganic water-soluble potassium polyphosphate salt; said first period of time being within the area designated ABCDA in FIGURE 1 and said second period of time being within the area EFGHIJE in FIGURE 1; the particular periods of time being dependent upon the specific viscosity within the range of from about 0.5 to about 3.5 of said copolymer of vinyl methyl ether and maleic anhydride.

3. A process as in claim 2, wherein the specific viscosity of said copolymer is between about 0.75 and about 1, said first period of time is from about 17.5 to about 22.5 minutes, and said second period of time is from about 22.5 to about 27.5 minutes.

4. A process as in claim 2, wherein the specific viscosity of said copolymer is between about 1 and about 1.25, said first period of time is from about 22.5 to about 27.5 minutes, and said second period of time is from about 18 to about 23 minutes.

5. A process as in claim 2, wherein the specific viscosity of said copolymer is between about 1.25 and about 1.50, said first period of time is from about 25 to about 30 minutes, and said second period of time is from about 15 to about 20 minutes.

6. A process as in claim 2, wherein the specific viscosity of said copolymer is between about 1.5 and about 1.75, said first period of time is from about 28 to about 33 minutes, and said second period of time is from about 12 to about 17 minutes.

7. A process as in claim 2, wherein the specific viscosity of said copolymer is between about 1.75 and about 2, said first period of time is from about 32 to about 37 minutes, and said second period of time is from about 7.5 to about 12.5 minutes.

8. A process as in claim 2, wherein the specific viscosity of said copolymer is between about 2 and about 2.25, said first period of time is from about 34 to about 39 minutes, and said second period of time is from about 6 to about 12 minutes.

9. A process as in claim 2, wherein the specific viscosity of said copolymer is between about 2.25 and about 2.5, said first period of time is from about 37 to about 42

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minutes, and said second period of time is from about 6 to about 12 minutes.

10. A process as in claim 2, wherein the specific viscosity of said copolymer is between about 2.5 and about 2.75, said first period of time is from about 39 to about 44 minutes, and said second period of time is from about 6 to about 12 minutes. 5

11. A process as in claim 2, wherein the specific viscosity of said copolymer is between about 2.75 and about 3, said first period of time is from about 42 to about 47 minutes, and said second period of time is from about 6 to about 12 minutes. 10

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References Cited

UNITED STATES PATENTS

3,235,505	2/1966	Tuvell	-----	252—135
3,328,309	6/1967	Grifo	-----	252—137

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