

"CONCENTRATED SINGLE-PHASE BUILT
LIQUID DETERGENT COMPOSITION"

The present invention relates to concentrated aqueous, built liquid detergent compositions suitable for laundry or pre-soak formulations. More particularly, it relates to aqueous built liquid detergent compositions which are highly concentrated in surfactant and builder and are provided as homogeneous, clear single-phase liquid solutions.

The formulation of concentrated built aqueous liquid detergent compositions has been a commercial objective in the detergent art in recent years. It is generally required that such compositions provide good detergency at low product concentration in the bath, contain water as the principal solvent and are in the form of homogeneous single-phase solutions which provide long-term shelf life without undergoing phase separation. Conventional liquid detergent compositions containing a detergency builder are generally not highly concentrated. That is, they are formulated as relatively dilute aqueous solutions so as to solubilize the builder and surfactant in the liquid composition. To provide the desired detergency, relatively high concentrations of such product are needed in the bath.

The term "concentrated" as used herein refers to liquid detergent compositions which can provide effective detergency at a product concentration equivalent to about "1/4 cup" under U.S. washing conditions, namely about 60 ml of detergent composition per standard wash load (about 17 U.S. gallons (64 litres) for a top loading washing machine), which

corresponds to a concentration of about 0.1% of the liquid detergent composition in the wash bath. To achieve a commercially acceptable level of detergency at such low product concentration, it is necessary that a high proportion of the detergent composition be comprised of active ingredients, notably, surfactant and builder. Thus, the term "concentrated" liquid detergent as used herein, is defined as a detergent composition which contains no more than about 65%, by weight, of water.

As a practical matter, it is important that water is used as the principal, if not the sole, solvent in such concentrated liquid detergent composition, avoiding the use of costly solvents such as glycols. Accordingly, the liquid detergent compositions described herein contain at a minimum about 35% water, by weight of the liquid composition, a water content of about 45% to 60% being ordinarily preferred.

Built liquid detergent compositions are known in the art. However, because of the limited solubility of builder and surfactant in water, such detergent compositions are generally prepared as relatively dilute aqueous compositions containing for the most part in excess of 65%, and often as high as 93%, by weight, water. Frequently, an alkylene glycol co-solvent is used to enhance the solubility of the built detergent composition. In those aqueous compositions which contain less than 65% water, the proportion of builder is generally kept low, i.e. no

- greater than about 10%, by weight, so as to enhance the solubility of the built detergent in water. To provide acceptable detergency when used under standard U.S. washing conditions, such known liquid compositions are conventionally used at product concentrations substantially above the "1/4 cup" concentration (about 0.1%, by weight) at which the liquid detergent compositions of the present invention are effective. Moreover, the conventional detergent compositions are generally in the form of emulsions or suspensions rather than forming clear homogeneous solutions which are stable against phase separation.

- The detergent compositions described in U.S. Patent No. 3,912,662 to Martinsson et al and U.S. Patent No. 4,021,377 to Borchert et al are illustrative of the prior art. The Martinsson et al patent discloses an aqueous detergent composition containing nonionic and betaine detergents and a polyphosphate builder. In Example 1, a composition is described containing 66% water and 12% alkylene glycol as the solvent. The Borchert et al patent describes a phosphate-free liquid detergent composition containing citrate builder and surfactant in a water-glycol solvent. The amount of water in each of the seven compositions disclosed in Table 1 of the patent is less than 26%, by weight, the major portion of the solvent being an alkylene glycol. Consequently, the ability to provide an economical liquid detergent composition which utilizes water as

the principal solvent yet is in the form of a concentrated clear single-phase solution remains as a problem yet to be overcome in formulating a commercially acceptable built concentrated liquid detergent composition.

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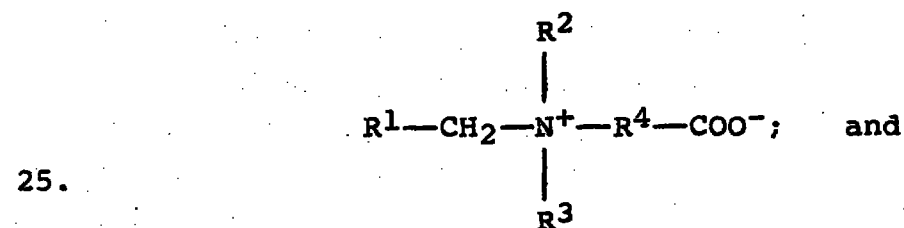
The present invention provides a concentrated aqueous single-phase homogeneous built liquid detergent composition comprising:

10. (a) from about 15 to 18%, by weight, of a water-soluble non-phosphate detergent builder salt;

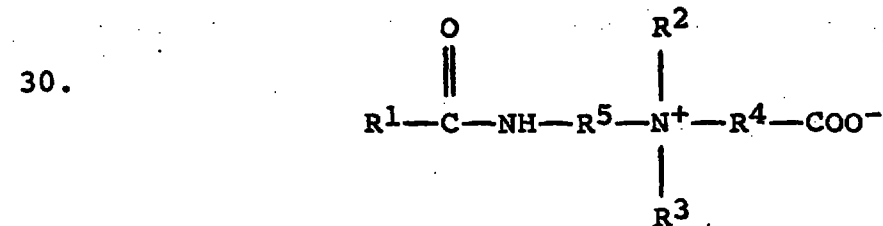
15. (b) from about 15 to 23%, by weight, of a surface active nonionic detergent compound which is the condensation product of 5 to 9 moles of ethylene oxide with one mole of an aliphatic alcohol containing 12 to 15 carbon atoms;

(c) from about 1 to 6%, by weight, of at least one amphoteric detergent compound selected from the group consisting of

20. (i) betaine detergent compounds having the structure:



(ii) alkyl amido betaine detergent compounds having the structure:



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wherein R^1 represents an alkyl group or a mixture of alkyl groups containing 9 to 13 carbon atoms, R^2 and R^3 each independently represent a methyl or an ethyl group, and R^4 and R^5 each independently represent a methylene, ethylene or propylene radical;

(d) from about 5 to 8%, by weight, of a solubilizer consisting essentially of an alkyl metal salt of octyl phosphonate; and

(e) from about 35 to 65%, by weight, water.

In accordance with the process aspects of the present invention, laundering of stained and/or soiled materials is effected by contacting such materials with an aqueous solution of the above-defined liquid detergent composition.

Unlike the built liquid detergent compositions known in the art, the compositions of the present invention contain a high concentration of builder and surfactant yet are characteristically clear, single-phase homogeneous solutions which are physically stable over prolonged periods of storage and over a wide range of temperature. The particular combinations of nonionic and betaine detergents with non-phosphate builder salt and solubilizer in accordance with the present invention unexpectedly form clear single-phase aqueous solutions, highly concentrated in both surfactant and builder. From a commercial standpoint, the compositions of the present invention are particularly advantageous insofar as they are

- phosphate-free in conformity with governmental regulations in many areas which prohibit the use of phosphate-containing detergents; they are relatively economical to formulate in that they utilize water as the principal solvent and avoid the use of costly co-solvents such as alkylene glycols in other than minor amounts; they provide effective detergency at low product concentrations in the wash bath, notably at a so-called 1/4 cup concentration, a desirably low concentration under U.S. washing conditions; and they are homogeneous solutions, avoiding problems of non-uniformity and phase separation associated with the storage and use of emulsions and dispersions.

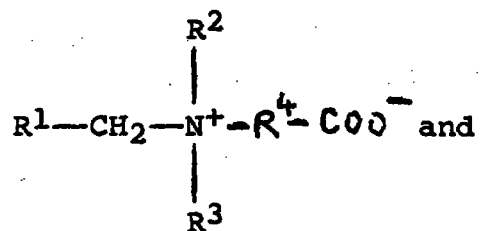
- The nonionic detergent compound in the liquid detergent compositions of the present invention may constitute from about 15 to 23%, and preferably from 17 to 19%, by weight, of the detergent composition, and the amphoteric detergent compound will generally vary from about 1 to 6%, preferably from 2 to 4%, by weight, of such compositions. The relative amounts of each of the aforementioned detergents is generally determined by the amount of builder salt employed. The higher the builder concentrations within the range of 15 to 18%, the lower the maximum concentration of nonionic detergent which may be employed in the composition and still form a stable single-phase solution. Conversely, at higher concentrations of builder salt, the concentration of amphoteric detergent and solubilizer is preferably increased within the ranges of concentration set forth above so as to

- solubilize the mixture and form a clear single-phase solution having the requisite detergency. Thus, for example, at a builder concentration of about 17% or above, the preferred concentration of nonionic surfactant is from about 16 to 18%, the amphoteric detergent is from about 2 to 4%, and most desirably at least 3%, and the concentration of solubilizer is about 7 to 8%, all percentages being by weight of the total composition.
5. The synthetic nonionic detergent employed in the practice of the present invention is specific to those compounds which are the condensation product of 5 to 9 moles of ethylene oxide with an aliphatic alcohol containing 12 to 15 carbon atoms. The
 15. aliphatic alcohol is preferably a straight chain alcohol, and most preferably is a fatty alcohol or mixture thereof containing an average of 12 to 13 carbon atoms per mole. The number of ethylene oxide groups per mole of alcohol preferably averages about
 20. 6.5 or 7. Neodol (Registered Trade Mark) 23-6.5 and Neodol (Registered Trade Mark) 25-7 are particularly preferred for use herein, both of such products being made by Shell Chemical Company, Inc.

The amphoteric detergent compounds most useful in the compositions of the present invention are the betaine and alkyl amido betaine detergent compounds having the following structures:

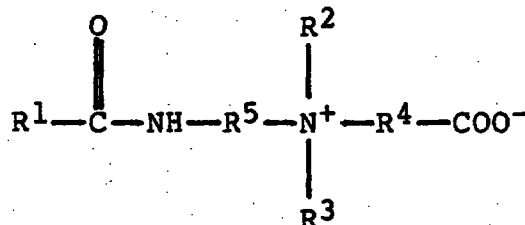
(i) betaine

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(ii) alkyl amido betaine



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wherein in each of the above structures R^1 represents an alkyl chain or a mixture of alkyls containing 9 to 13 carbon atoms; R^2 and R^3 each independently represent a methyl or an ethyl group; and R^4 and R^5 each independently represent a methylene, ethylene or propylene radical.

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When R^1 is a mixture of alkyls of varying chain length, it is preferred that such mixture be comprised predominantly of alkyls having 9 to 13 carbon atoms, although it is sufficient, albeit less preferred, if only the predominant alkyl in the mixture contains 9 to 13 carbon atoms and the remaining alkyl chains are outside of such range. R^1 is preferably derived from coconut oil.

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R^2 and R^3 are preferably methyl groups and R^4 preferably a methylene group and R^5 is preferably a propylene radical. Accordingly, preferred betaines for use herein are cocodimethylammonium acetate (cocobetaine) and cocoamidopropyl dimethylammonium acetate (cocoamido betaine).

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An anionic detergent may optionally be employed in minor amounts to supplement the nonionic and amphoteric detergent compounds in the liquid deter-

gent compositions of the present invention.

Generally, the amount of anionic detergent will be below about 3%, by weight, of the total composition because of the limited solubility of such detergents

5. in the built liquid detergent composition. Alkyl benzene sulphonate salts wherein the alkyl group contains 10 to 18 carbon atoms are particularly limited in solubility in the compositions of the present invention, and hence it is preferred that the
10. compositions of the present invention be substantially free of such compounds to avoid the possibility of product separation.

The preferred anionic detergents for use herein are sulphated ethoxylated higher fatty alcohols of

15. the formula



wherein R represents a fatty alkyl group of from 10 to 18 or 20 carbon atoms, m is from 2 to 6 or 8

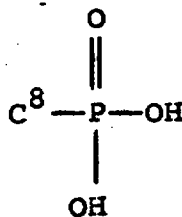
- (preferably having a value from about 1/5 to 1/2 the
20. number of carbon atoms in R) and M is a solubilizing salt-forming cation, such as an alkali metal, ammonium, lower alkyl-amino or lower alkanolamino. A preferred polyethoxylated alcohol sulphate detergent is available from Shell Chemical Company and is
25. marketed as Neodol 25-3S.

- Water is the principal solvent in the concentrated liquid detergent compositions of the present invention. The concentration of water may vary from about 35 to 65%, with a concentration in the range of
30. 45 to 60%, by weight, being generally preferred. A

- co-solvent such as an alkylene glycol, e.g. ethylene glycol or propylene glycol, may optionally be employed in minor amounts for the purpose of enhancing the solubility of the surfactant and the builder in solution. The concentration of alkylene glycol in the detergent composition should, if present, be below about 10%, by weight, of the total composition, preferably below about 5%, and most preferably, the composition is substantially free of such alkylene glycol.

- An alkali metal salt of octyl phosphonate is included in the detergent composition because of its solubilizing properties with respect to nonionic surfactants and builder salt. Such solubilizer is used in an amount of from 5 to 8%, by weight, of the total composition, a concentration of at least 7% being preferred when the builder salt concentration is about 17% or higher.

- The term octyl phosphonate as used herein means a compound having the formula



- wherein C^8 represents an eight carbon atom member aliphatic chain, preferably an alkyl chain.

- The non-phosphate detergent builder salts are employed in the present compositions in amounts generally of from about 15 to 18%, by weight.

Specific examples of non-phosphate water-soluble inorganic builders include water-soluble inorganic carbonate, bicarbonate and silicate salts. The alkali (for example, sodium and potassium)

5. carbonates, bicarbonates and silicates are particularly useful herein.

Water-soluble organic builders are also useful and include the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxysulphonates.

10. Specific examples of polyacetate and polycarboxylate builders include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine-tetracetic acid, nitrilotriacetic acid, benzene polycarboxylic (i.e. penta- and tetra-) acids, carboxymethoxysuccinic acid and citric acid. As used herein, the term "builder" does not include surfactants and soaps such as the water-soluble salts of higher fatty acids containing from about 8 to 20 carbon atoms.
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The optical fluorescent brighteners or whiteners often employed in the liquid detergent compositions are important constituents of modern detergent compositions which give washed laundry and materials a bright appearance so that the laundry is not only clean but also appears clean. Although it is possible to utilize a single brightener for a specific intended purpose in the liquid detergent compositions of the present invention it is generally desirable to employ mixtures of brighteners which

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will have good brightening effects on cotton, nylons, polyesters and blends of such materials and which are also bleach stable. A good description of such types of optical brighteners is given in the article "The Requirements of Present day Detergent Fluorescent Whitening Agents" by A.E. Siegrist, J. Am. Oil Chemists Soc., January 1978 (Vol. 55). That article and U.S. Patent 3,812,041, issued 21st May, 1974, both of which are hereby incorporated by reference contain detailed descriptions of a wide variety of suitable optical brighteners.

Among the brighteners that are useful in the liquid detergent compositions of the present invention are: Calcofluor 5 BM (American Cyanamid); Tinopal (Registered Trade Mark) LPW (Ciba); SOF A-2001 (Ciba); CDW (Hilton-Davis); Phorwhite RKH, Phorwhite BBH and Phorwhite BHC (Verona); CSL, powder, acid (American Cyanamid); FB 766 (Verona); Blancophor PD (GAF); UNPA (Geigy); Tinopal RBS 200 (Geigy).

Adjuvants may be present in the liquid detergent compositions to provide additional properties, either functional or aesthetic. Included among the useful adjuvants are soil suspending or anti-redeposition agents, such as polyvinyl alcohol, sodium carboxymethyl cellulose, hydroxypropylmethyl cellulose; thickeners, e.g. gums, alginates, agar agar; foam improvers, e.g. lauric myristic diethanolamide; foam destroyers, e.g. silicones; bactericides, e.g. tribromosalicylanilide, hexachlorophene; dyes; pigments (water dispersible); preservatives; ultra-

- violet absorbers; fabric softeners; enzymes; opacifying agents, e.g. polystyrene suspensions; and perfumes. Of course, such materials will be selected based on the properties desired in the finished product, their compatibility with the other constituents, and their solubility in the liquid composition.
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- The liquid compositions of the present invention are efficient and easy to use. Compared to heavy duty laundry detergent powders, much smaller volumes of the liquids of the present invention are employed to obtain comparable cleaning of soiled laundry. For example, using a typical preferred formulation of the present invention, only about 71 grams or 1/4 cup of liquid is needed for a full tub of wash in a top-loading automatic washing machine in which the water volume is about 17 gallons (about 64 litres); and even less is needed for front-loading machines. Thus, the concentration of the liquid detergent composition in the wash water is of the order of about 0.1%. Usually, the proportion of the liquid composition in the wash solution will range from about 0.05 to 0.3%, preferably from 0.10 to 0.20%. The proportions of the various constituents of the liquid composition may vary accordingly. Equivalent results can be obtained by using greater proportions of a more dilute formulation but the greater quantity needed will require additional packaging and will generally be less convenient for consumer use.
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30. The invention may be put into practice in

various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

EXAMPLE 1

5. A concentrated built liquid detergent composition in accordance with the present invention was formulated as set forth in Table 1 below. The percentages shown refer to the 100% active component.

TABLE 1

10.	<u>COMPONENT</u>	<u>WEIGHT PERCENT</u>
	Sodium Citrate	17.2
	Ethoxylated C ₁₂ -C ₁₃ alcohol (6.5 moles EO/mole alcohol)	17.6
	Cocoamido betaine ⁽¹⁾	3.1
15.	Octyl phosphonate ⁽²⁾ (Potassium salt)	7.0
	Brightener and blue dye	0.2
	Water	Balance

Notes on Table 1

- (1) Provided as "Varion CADG", an aqueous solution of cocoamido betaine sold by Sherex Chemical Company.
20. (2) The phosphonate is provided as "Hoe S-2413" sold by American Hoechst Company, which is then reacted with potassium hydroxide to form the potassium salt.
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The above-described liquid composition was a clear blue-coloured single-phase homogeneous liquid detergent having a viscosity of about 80 centipoise (cp) at 75°F (24°C), and which poured satisfactorily

- from a plastic detergent bottle with a discharge opening of about 2.5 cm diameter. The liquid detergent was employed to wash a mixed load of soiled laundry which included cotton swatches and polyester/
5. cotton swatches soiled with particulate soil and with sebum soil. The wash temperature was 120°F (49°C) and the concentration of the liquid detergent in the wash bath was about 0.1%, by weight. After washing, the laundered items were rinsed in tap water and then
10. dried. The degree of stain removal was measured by taking a reflectance reading for each stained test swatch prior to and after the washing using a Gardner XL-20 colourimeter.

- The laundering operation described above was
15. repeated with a control detergent, a commercial aqueous built liquid detergent composition containing 19% dodecylbenzene sulphonate, 10% sodium citrate, 7% ethoxylated alcohol surfactant, and 5% sodium toluene sulphonate hydrotrope used at a "1/2 cup" concentra-
20. tion of about 0.2%, by weight, in the bath. The detergency of both compositions was compared based on the measured stain removal achieved during laundering. The detergency of the liquid detergent of the present invention at a "1/4 cup" concentration was shown to
25. be either equivalent to or superior to that achieved with the control liquid detergent at a "1/2 cup" concentration with respect to laundered soiled and stained fabrics.

EXAMPLES 2A and 2B

- The effect of incorporating a betaine detergent not in accordance with the present invention into a built liquid detergent composition containing
5. nonionic surfactant and a high concentration of builder was demonstrated by preparing two liquid compositions as described in Example 1, except that the cocoamido betaine in the composition of Example 1
10. was replaced in one composition by stearyl betaine (Example 2A) and in the second composition by palmytyl betaine (Example 2B). Both of the resulting compositions were unstable and formed separate phases in contrast to the stable clear solution which characterised the composition of Example 1.

15. EXAMPLES 3A and 3B

Detergency tests were conducted with compositions A and B formulated as shown in Table 2 below. The numbers in Table 2 represent the percent by weight of each component in the liquid composition.

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TABLE 2

<u>EXAMPLE</u>	<u>3A</u>	<u>3B</u>
<u>COMPONENT</u>		
Sodium citrate	17.2	17.2
Ethoxylated C ₁₂ -C ₁₃ alcohol	17.6	22.0
25. (6.5 moles EO/mole alcohol)		
Cocoamido betaine	3.1	--
Octyl phosphonate (potassium salt)	7.0	14.0
Water	Balance	Balance

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The compositions of Examples 3A and 3B were clear, single-phase solutions. The composition of Example 3A is a composition in accordance with the present invention substantially as previously described in Example 1. The composition of Example 3B represents the best performing formulation from the standpoint of detergency measured at a concentration of 0.1% in the bath from among compositions containing the same components of the composition of Example 3A except for the omission of a betaine detergent, and which formed a clear single-phase solution. The composition of Example 3B is not in accordance with the present invention and is a comparison example.

The detergency of the composition of Examples 3A and 3B was determined in a Tergotometer vessel manufactured by U.S. Testing Company on the test fabrics and under the conditions stated in Table 3 below:

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TABLE 3TEST FABRICS

TFN - Test fabric soil on Nylon
PCC - Piscataway clay on cotton
TFC - Test fabric soil on cotton
25 PCDC - Piscataway clay on Dacron (Registered Trade Mark)/cotton
EMPA - EMPA 101 on heavy cotton

WASH CONDITIONS

Liquid detergent concentration 0.10%
30 Water temperature 120°F (49°C)
Water hardness about 150 ppm as calcium carbonate

At the end of the wash, the test swatches were rinsed in tap water and then dried. A reflectance reading was taken for each test swatch prior to and after the washing using a Gardner XL-20 colourimeter.

5. The values for the change in reflectance (ΔR_d) are shown below in Table 4 for each of the aforementioned test fabrics. A difference greater than 0.8 between two values of ΔR_d is considered significant for all washed test fabrics except for measurements on EMPA and PCDC where only ΔR_d values above 1.3 are considered significant.

TABLE 4
 ΔR_d Values for Fabrics Washed with
Compositions A, B and C

15.	<u>FABRIC</u>	<u>TFN</u>	<u>PCC</u>	<u>EMPA</u>	<u>TFC</u>	<u>PCDC</u>
	<u>EXAMPLE</u>					
	3A	38	25	18	8	32
	3B	35	24	17	8	33

20. Table 4 demonstrates the unexpected improved detergency attendant on the use of a composition in accordance with the present invention relative to a single-phase liquid detergent composition similar thereto but which was not formulated in accordance with the present invention. The composition of Example 3A is shown to be superior to the composition of Example 3B with respect to two of the five test fabrics laundered; and essentially equivalent in detergency with respect to the other three test fabrics laundered above.
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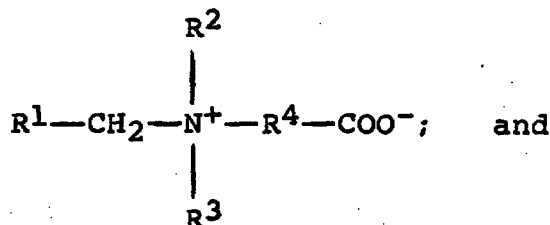
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CLAIMS

1. A concentrated aqueous single-phase homogeneous built liquid detergent composition comprising:

- (a) from about 15 to 18%, by weight, of a water-soluble non-phosphate detergent builder salt;
5. (b) from about 15 to 23%, by weight, of a surface active nonionic detergent compound which is the condensation product of 5 to 9 moles of ethylene oxide with one mole of an aliphatic alcohol containing 12 to 15 carbon atoms;
10. (c) from about 1 to 6%, by weight, of at least one amphoteric detergent compound selected from the group consisting of
- (i) betaine detergent compounds having the structure:

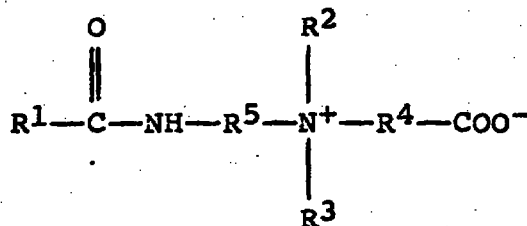
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- (ii) alkyl amido betaine detergent compounds having the structure:

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wherein R¹ represents an alkyl group or a mixture of alkyl groups containing 9 to 13 carbon

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atoms, R^2 and R^3 each independently represent a methyl or an ethyl group and R^4 and R^5 each independently represent a methylene, ethylene or propylene radical;

5. (d) from about 5 to 8%, by weight, of a solubilizer consisting essentially of an alkali metal salt of octyl phosphonate; and
(e) from about 35 to 65%, by weight, water.

10. 2. A detergent composition as claimed in Claim 1 in which the said nonionic detergent compound is the condensation product of 6 to 7 moles of ethylene oxide with one mole of an aliphatic alcohol containing 12 to 13 carbon atoms.

15. 3. A detergent composition as claimed in Claim 1 or Claim 2 in which the said builder salt is sodium citrate.

20. 4. A detergent composition as claimed in Claim 1, 2 or 3 in which R^1 in the structures of the said betaine detergent compounds is derived from coconut oil, R^2 and R^3 each represent a methyl group, and R^4 represents a methylene radical.

25. 5. A detergent composition as claimed in any one of Claims 1 to 4 in which the said betaine detergent compound is cocoamidopropyldimethyl ammonium acetate.

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6. A detergent composition as claimed in any one of Claims 1 to 5 which contains less than about 3%, by weight, of a surface active anionic detergent compound.
5. 7. A detergent composition as claimed in any one of Claims 1 to 6 which is substantially free of a C₁₀-C₁₈ alkyl benzene sulphonate anionic detergent.
10. 8. A detergent composition as claimed in any one of Claims 1 to 7 which contains less than about 10%, by weight, of an alkylene glycol.
15. 9. A detergent composition as claimed in any one of Claims 1 to 8 which is substantially free of an alkylene glycol.
20. 10. A detergent composition as claimed in any one of Claims 1 to 9 which contains from about 45 to 60%, by weight, of water.
25. 11. A detergent composition as claimed in any one of Claims 1 to 10 in which the concentration of the builder salt is about 17% and the nonionic detergent compound is present in an amount of from about 16 to about 18%, by weight, of the composition.
30. 12. A detergent composition as claimed in any one of Claims 1 to 11 in which the concentration of the said solubilizer in the composition is about 7%, by weight.



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13. A detergent composition as claimed in Claim 1 substantially as specifically described herein with reference to Example 1 or Example 3A.

5. 14. A method of laundering comprising contacting the stained and/or soiled fabrics to be laundered with a concentrated aqueous single-phase homogeneous liquid detergent composition as claimed in any one of Claims 1 to 13.

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15. A method as claimed in Claim 14 in which the concentration of detergent composition in the wash water is about 0.1%, by weight.

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