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DETERGENT COMPOSITIONS CONTAINING
REVERSED ZWITTERIONIC PHOSPHORUS
COMPOUNDS

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Int. Cl. C11d 3/30, 3/34, 3/36

U.S. Cl. 252-152

4 Claims

ABSTRACT OF THE DISCLOSURE

Detergent compositions containing reversed zwitterionic compounds having a negatively charged center adjacent a hydrophobic chain and a positively charged center removed by 2 to about 4 carbon atoms from the negatively charged center are disclosed. These compounds have the formula $R-Z-R^1-X$ wherein R is an aliphatic radical, e.g., alkyl or alkenyl, containing from about 10 to about 20 carbon atoms; Z is a negatively charged radical selected from the group consisting of phosphate, phosphonate, and phosphinate radicals; R^1 is an alkylene radical containing from 2 to about 4 carbon atoms; and X is a positively charged radical selected from the group consisting of ammonium and tertiary sulfonium radicals; said ammonium radical having the formula



wherein R^2 , R^3 and R^4 are selected from the group consisting of hydrogen, methyl, and ethyl; said tertiary sulfonium radical having the formula



wherein R^5 and R^6 are selected from the group consisting of methyl and ethyl.

This application is a division of U.S. patent application Ser. No. 584,099, filed Oct. 4, 1966, now Pat. No. 3,507,937, in the name of Roger E. Zimmerer and entitled Reversed Zwitterionic Phosphorus Compounds.

This invention relates to novel zwitterionic detergent compounds and to detergent compositions containing these compounds. These compounds have a negatively charged center adjacent a hydrophobic chain, and a positively charged center removed by 2 to about 4 carbon atoms from this negatively charged center. These compounds are characterized herein as being reversed zwitterionic compounds to distinguish them from more conventional zwitterionic compounds in which a positively charged center is adjacent the hydrophobic chain, and a negatively charged center is removed by two or more carbon atoms from this positively charged center.

There are several properties that are regarded as being essential for a compound to be suitable for use as a detergent. Foremost, is the cleaning ability of the compound, i.e., its ability to remove soil, e.g., from soiled clothes. In addition, the detergent should remain in active form under conditions of usage, e.g., at high temperatures such as 140° F. and in aqueous solutions. Although there are a number of organic detergents which have these properties, detergent compounds such as those of the present invention which have additional desirable properties find wider scope of application.

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The novel reversed zwitterionic compounds of this invention clean as well as tetrapropylenebenzenesulfonate. They remain in active form during conditions ordinarily encountered during washing. In addition, they remain in active form when mixed with builders and with anionic, nonionic, cationic, ampholytic, and zwitterionic detergents. Moreover, anionic brighteners remain in active form when mixed with the present reversed zwitterionic detergent compounds.

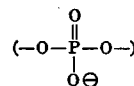
The reversed zwitterionic compounds of this invention have the formula $R-Z-R^1-X$ wherein R is an aliphatic radical, e.g., alkyl or alkenyl containing from about 10 to about 20 carbon atoms; Z is a negatively charged radical selected from the group consisting of phosphate, phosphonate, and phosphinate radicals; R^1 is an alkylene radical containing from 2 to about 4 carbon atoms; and X is a positively charged radical selected from the group consisting of ammonium and tertiary sulfonium radicals; said ammonium radical having the formula



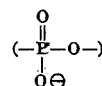
wherein R^2 , R^3 and R^4 are selected from the group consisting of hydrogen, methyl, and ethyl; said tertiary sulfonium radical having the formula



wherein R^5 and R^6 are selected from the group consisting of methyl and ethyl. The phosphate radical herein has the formula



The phosphate radical herein has the formula



The phosphinate radical herein has the formula



R^2 , R^3 , and R^4 can be the same or different within the same molecule. R^5 and R^6 can be the same or different within the same molecule.

For purposes of organization and convenience the above compounds wherein R^2 , R^3 , or R^4 are hydrogen are termed zwitterionics herein. These compounds might more appropriately be classified as ampholytics since they deprotonate to the extent of one hydrogen over a wide pH range, including the alkaline pH range, forming the corresponding compounds containing an amino moiety. Thus, in detergent compositions containing water or moisture or under conditions of usage, these compounds are present in ampholytic form. They, however, may be isolated in zwitterionic form and are ordinarily in this form at the instant of preparation of the detergent composition containing them.

Reversed zwitterionic detergent compounds, none of which are known to be described in the prior art, and exemplary of those within the scope of the present invention are set forth in Table I below wherein R, Z, R^1 , X, R^2 , R^3 , R^4 , R^5 , and R^6 are applied in the formulas set forth above.

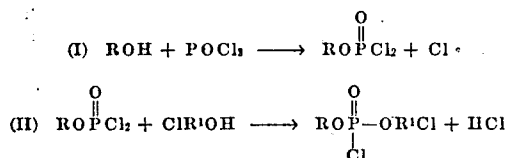
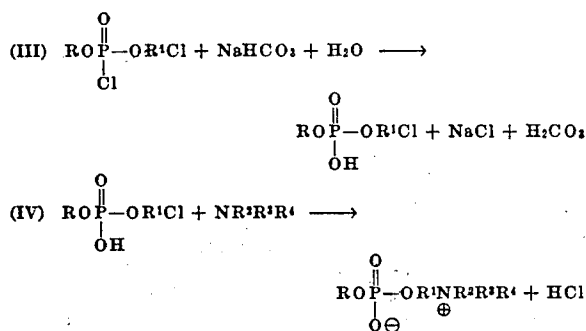
TABLE I

	R	Z	R ¹	X	R ²	R ³	R ⁴	R ⁵	R ⁶
1.	Decyl	Phosphate	Ethylene	Ammonium	Methyl	Methyl	Methyl		
2.	Dodecyl	do	do	do	do	do	do		
3.	Tetradecyl	do	Trimethylene	do	do	do	Ethyl		
4.	Octadecyl	do	Tetramethylene	do	Hydrogen	do	Methyl		
5.	do	do	Ethylene	Tertiary sulfonium				Ethyl	Ethyl
6.	Decyl	Phosphonate	Tetramethylene	do				Methyl	Do.
7.	Dodecyl	do	Ethylene	Ammonium	Methyl	Methyl	Methyl		
8.	do	do	Trimethylene	do	Ethyl	Ethyl	Ethyl		
9.	do	do	Ethylene	do	Hydrogen	Methyl	Methyl		
10.	Tridecyl	do	do	do	do	do	Ethyl		
11.	Hexadecyl	do	Tetramethylene	Tertiary sulfonium				Methyl	Methyl
12.	Oleyl	do	Ethylene	Ammonium	Methyl	Ethyl	Ethyl		
13.	Elcosyl	do	do	do	Hydrogen	Hydrogen	Hydrogen		
14.	Decyl	Phosphinate	Tetramethylene	do	do	do	Methyl		
15.	Dodecyl	do	Ethylene	do	Methyl	Methyl	do		
16.	do	do	do	Tertiary sulfonium				Methyl	Do.
17.	Hexadecyl	do	Trimethylene	Ammonium	Methyl	Methyl	Methyl		
18.	Octadecyl	do	Ethylene	do	Hydrogen	Ethyl	Ethyl		
19.	do	do	do	do	do	Methyl	do		
20.	Elcosyl	do	do	do	do	Hydrogen	do		
21.	Dodecyl	Phosphate	do	do	do	Methyl	Methyl		

Preferred reversed zwitterionics of this invention are those compounds wherein R defined generally above contains from 12 to 16 carbon atoms, and X defined generally above is a quaternary ammonium radical or an ammonium radical containing only one hydrogen. The most preferred compounds are Compounds 7 and 9 in Table I above, i.e., 2-(trimethylammonio)ethyl dodecylphosphonate and 2-(dimethylammonioethyl) dodecylphosphonate, respectively.

The compounds of the present invention can be prepared according to the following reaction equations wherein R, Z, R¹, X, R², R³, R⁴, R⁵ and R⁶ are defined as hereinbefore except as specified otherwise hereinafter.

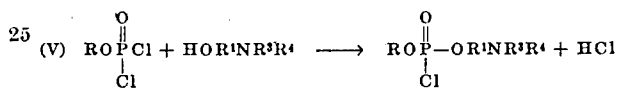
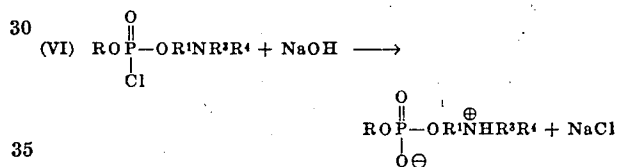
Compounds wherein Z is phosphate and X is ammonium wherein R² and R³ are hydrogen and R⁴ is hydrogen, methyl, or ethyl



In Equation IV, R² and R³ are each hydrogen, and R⁴ is hydrogen, methyl, or ethyl. These reactions can be carried out under the following conditions:

Reaction:	Solvent	Temperature, ° C.	Time
I.	Ethylene dichloride	25-40	2 hours to 4 hours.
II.	do	25-40	Do.
III.	Acetone	30-50	30 mins. to 1 hour.
IV.	Methanol	50-80	1 hour to 3 hours.

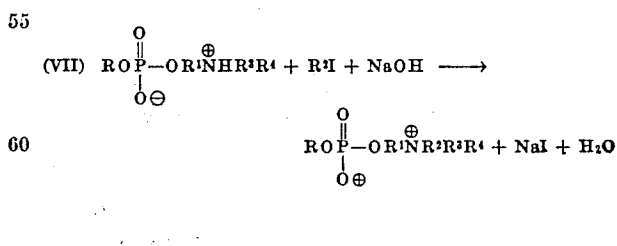
20 Compounds wherein Z is phosphate and X is ammonium wherein R² is hydrogen and R³ and R⁴ are methyl or ethyl



In these equations R³ and R⁴ are each methyl or ethyl, and neither of them is hydrogen. The alkyl dichlorophosphate in Reaction V can be made by the process of Reaction I hereinbefore. Reactions V and VI can be carried out under the following conditions:

Reaction:	Solvent	Temperature, ° C.	Time
V.	Ethylenedichloride	25-40	2 hours to 4 hours.
VI.	Methanol	25-30°	15 mins. to 45 mins.

Compounds wherein Z is phosphate and X is quaternary ammonium



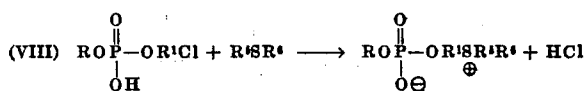
65 In this equation R², R³ and R⁴ are each methyl or ethyl, and none of them is hydrogen. The dialkylammonioalkyl alkylphosphate reactant in this equation can be made by

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the process of Reaction VI. Reaction VII can be carried out under the following conditions:

Reaction ----- VII.
Solvent ----- Dioxane.
Temperature ----- Reflux (about 105° C. for dioxane). 5
Time ----- 15 mins.-45 mins.

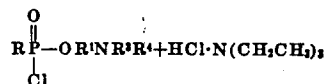
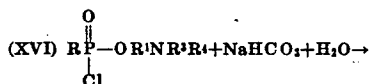
Compounds wherein Z is phosphate and X is tertiary sulfonium 10



The phosphate reactant in the equation of Reaction VIII can be made by the process of Reaction III hereinbefore. Reaction VIII can be carried out under the following conditions: 20

Reaction ----- VIII.
Solvent ----- Ethylene dichloride.
Temperature ----- 50° C.-100° C.
Time ----- 15 mins.-2 hours. 25

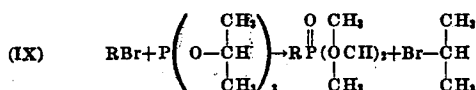
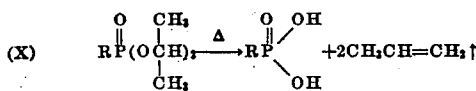
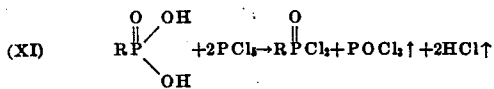
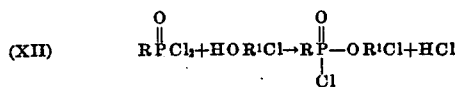
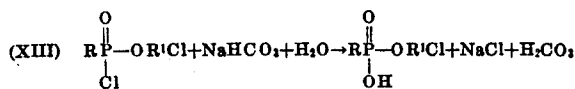
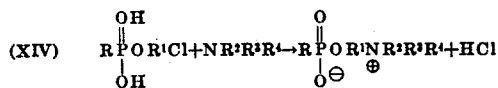
Compounds wherein Z is phosphonate and X is ammonium wherein R² is hydrogen and R³ and R⁴ are methyl or ethyl



In these equations R³ and R⁴ are each methyl or ethyl, and neither of them is hydrogen. The phosphonic dihalide reactant in Reaction XV can be made by the process of Reaction XI. Reactions XV and XVI can be carried out under the following conditions:

Reaction:	Solvent	Temperature, ° C.	Time
XV	Ethylene dichloride	20-60	15 mins. to 2 hours.
XVI	Acetone	30-50	30 mins. to 1 hour.

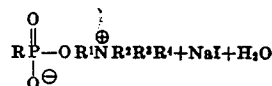
Compounds wherein Z is phosphonate and X is ammonium wherein R² and R³ are hydrogen and R⁴ is hydrogen, methyl, or ethyl



These reactions can be carried out under the following conditions: 65

Reaction:	Solvent	Temperature, ° C.	Time
IX	Excess trialkylphosphite	140-150	4 hours to 8 hours.
X	None	170-270	15 mins. to 1 hour.
XI	do	90-100	1 hour to 2 hours.
XII	Ethylene dichloride	25-40	2 hours to 4 hours.
XIII	Acetone	30-50	30 mins. to 1 hour.
XIV	Methanol	50-80	1 hour to 3 hours.

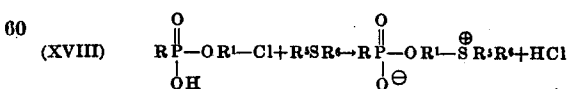
Compounds wherein Z is phosphonate and X is quaternary ammonium



In this equation R², R³ and R⁴ are each methyl or ethyl, and none of them is hydrogen. The dialkylammonioalkyl alkylphosphonate reactant in this equation can be made by the process of Reaction XVI. Reaction XVII can be carried out under the following conditions:

Reaction ----- XVII.
Solvent ----- Ethyl alcohol.
Temperature ----- 50° C.-80° C.
Time ----- 3-6 hours. 55

Compounds wherein Z is phosphonate and X is tertiary sulfonium



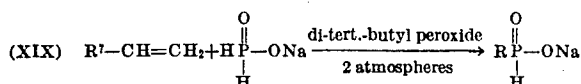
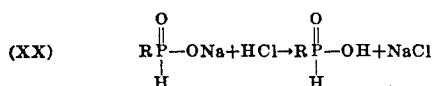
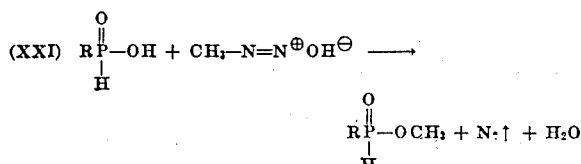
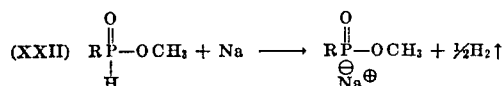
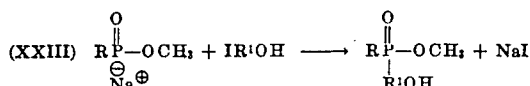
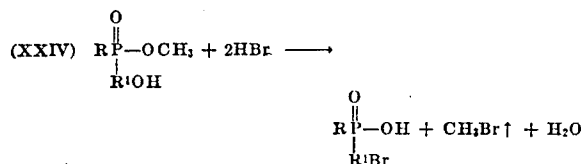
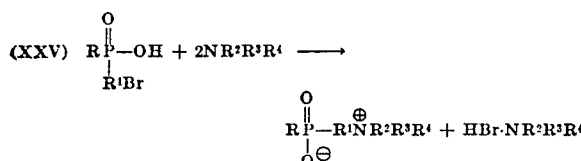
The phosphonate reactant in the equation of Reaction XVIII can be made by the process of Reaction XIII here-

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inbefore. Reaction XVIII can be carried out under the following conditions:

Reaction XVIII.
Solvent Ethylene dichloride.
Temperature 50° C.-100° C.
Time 15 mins.-2 hours.

Compounds wherein Z is phosphinate and X is ammonium wherein R² and R³ are hydrogen and R⁴ is hydrogen, methyl, or ethyl



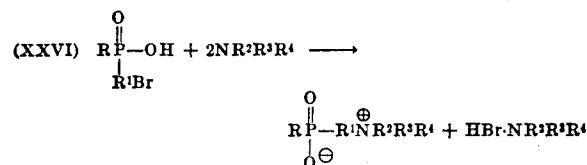
In Equation XIX, R¹ is an aliphatic radical containing two less carbon atoms than the desired R. In Equation XXV, R² and R³ are each hydrogen, and R⁴ is hydrogen, methyl or ethyl. Reactions XIX-XXV can be carried out under the following conditions:

Reaction:	Solvent	Temperature, ° C.	Time
XIX.....	Methanol.....	110-130	10-20 hours.
XX.....	Water/diethyl ether.....	20-35	5 minutes.
XXI.....	Diethyl ether.....	0-10	10-30 minutes.
XXII.....	Toluene.....	25-30	3-5 hours.
XXIII.....	do.....	Reflux ¹	2-4 hours.
XXIV.....	Petroleum ether.....	50-60	4-6 hours.
XXV.....	Acetone.....	Reflux ²	5-10 hours.

¹ About 10° C. for toluene.

² About 56° C. for acetone.

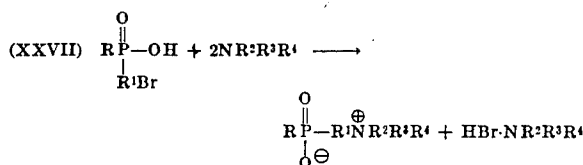
Compounds wherein Z is phosphinate and X is ammonium wherein R² is hydrogen and R³ and R⁴ are methyl or ethyl



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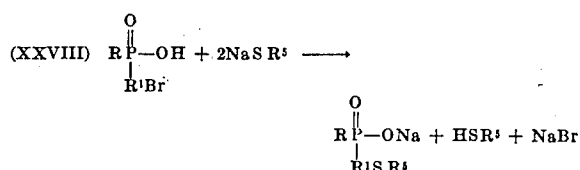
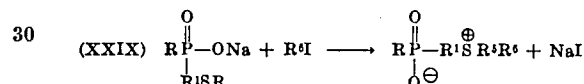
In this equation, the phosphinic acid reactant can be made by the process of Reaction XXIV; R² is hydrogen and R³ and R⁴ are each methyl or ethyl. This reaction can be carried out under the same conditions as Reaction XXV.

Compounds wherein Z is phosphinate and X is quaternary ammonium



15 In this equation, the reactant can be made by the process of Reaction XXIV, and R², R³, and R⁴ are each methyl or ethyl, and none of them is hydrogen. This reaction can be carried out under the same conditions as Reaction XXV.

20 Compounds wherein Z is phosphinate and X is tertiary sulfonium



The phosphinic reactant in Reaction XXVII can be made by the process of Reaction XXV hereinbefore. Reactions XXVIII and XXII can be carried out under the following conditions:

Reaction:	Solvent	Temperature, ° C.	Time, hours
XXVIII.....	Dioxane.....	25-50	15-20
XXIX.....	do.....	1 Reflux	1-10

¹ 101° C. for dioxane.

45 The following examples illustrate the preparation of the compounds of this invention.

EXAMPLE I

Diisopropyl dodecylphosphonate was prepared by reacting dodecyl bromide and triisopropyl phosphite according to the technique described in Ford-Moore and Williams, Journal of the Chemical Society 1947, p. 1465. This reaction was carried out at a temperature of 145° C. and

for a time period of 5 hours. The formed diisopropyl dodecylphosphonate is converted to dodecylphosphonic acid using the pyrolytic method described in the copending application of Roy, Ser. No. 218,863, filed Aug. 23, 1962 and now abandoned.

196 grams (0.78 mole) dodecylphosphonic acid was placed in a 1-liter flask. This flask was then placed on a steam bath. To this flask on the steam bath was added over a 15-minute period 360 grams (1.7 moles) PCl₅. This addition was carried out under dry nitrogen. The formed

mixture was maintained on the steam bath for one hour after the PCl_5 addition was completed. During the PCl_5 addition and thereafter the temperature of the mixture was maintained at $90^\circ\text{--}100^\circ\text{C.}$ by the steam bath. The flask was then removed from the steam bath. The excess PCl_5 in the reaction mixture was then converted to POCl_3 by rapidly passing SO_2 into the reaction mixture for 90 minutes. The POCl_3 and SOCl_2 in the mixture were then removed from the mixture under vacuum, and the residue was distilled to yield 210 grams (0.73 mole) of substantially pure dodecylphosphonic dichloride, having a boiling point ranging from 117°C. to 119°C. at 0.1 mm. Hg.

400 ml. of triethylamine having been dried over CaSO_4 was then introduced into a 1-liter, 3-necked, round-bottom flask, equipped with a thermometer, a condenser protected with a drying tube, an addition funnel, and a mechanical stirrer. Then, 143.5 grams (0.5 mole) of dodecylphosphonic dichloride was added to the flask with stirring over a 45-minute period. Next, 44.5 grams (0.5 mole) of 2-dimethylaminoethanol was added to the flask dropwise with stirring over a 30-minute period. During the 2-dimethylaminoethanol addition period, the reaction mixture in the flask was maintained at $40^\circ\text{--}50^\circ\text{C.}$ by cooling. After addition of the 2-dimethylaminoethanol was completed, the reaction mixture in the flask was stirred for one additional hour at 45°C. The reaction mixture was then allowed to cool to room temperature.

To this reaction mixture at room temperature was added dropwise, with stirring, over a 30-minute period, 20 ml. (1.1 mole) of water. During the water addition, the temperature of the reaction mixture rose rapidly, and was maintained at about 60°C. by means of a cold water bath. After the 30-minute water addition period, 180 ml. of water was poured into the reaction mixture to effect complete solution of the reaction mixture.

To this solution was added 1 liter of water containing 60 grams (1.5 moles) of sodium hydroxide. This addition was carried out by pouring the sodium hydroxide solution into the reaction solution. The temperature of the formed solution was about 35°C. during and after sodium hydroxide addition. The formed solution was evaporated on a steam bath under a current of nitrogen. The residue resulting from this evaporation was digested in 1 liter of boiling chloroform, and the insoluble materials were then removed by filtration. The chloroform was then evaporated on a steam bath under a current of nitrogen. The 160-gram residue was an extremely viscous, amber paste that was hygroscopic. This material was equilibrated with the atmosphere over a saturated solution of KSCN at room temperature yielding 172 grams of clear amber gel. Analysis of the gel showed it to be a mixture containing 90% by weight 2-(dimethylammonio)ethyl dodecyl phosphonate, i.e., Compounds 9 in Table I hereinbefore, and 10% by weight water.

Into a 1-liter, 3-necked, round-bottom flask, equipped with a heating mantle, a reflux condenser, and a mechanical stirrer, was charged 110 grams of the above gel [0.34 mole 2-(dimethylammonio)ethyl dodecylphosphonate] dissolved in 500 ml. of denatured ethyl alcohol. To this solution was added 52.5 grams (0.37 mole) of methyl iodide. This addition was carried out over a 10-minute period. During this addition the formed mixture was maintained at a temperature of $60^\circ\text{--}70^\circ\text{C.}$ After this addition, the mixture was brought to reflux temperature, i.e., about 78°C. , and was stirred at reflux temperature for four hours. At this point, the reflux condenser was replaced with a distillation head and condenser, and 350 ml. of alcohol was removed by distillation. To the resulting mixture was added with stirring 340 ml. of 1 N NaOH (0.34 mole NaOH). This addition was carried out all at once. During this addition the temperature of the mixture was maintained at $70^\circ\text{--}80^\circ\text{C.}$ The solvent in the mixture was then evaporated on a steam bath. To the residue was added 1000 ml. water to form a reaction solution. This solution was mixed with about 0.5 equivalents of cation

exchange resin in the hydrogen form and with about 0.5 equivalent of anion exchange resin in the hydroxide form. After about 30 minutes during which the mixture was periodically shaken, the resin was removed by filtration. The water in the filtrate was evaporated on a steam bath to provide an amber solid which was equilibrated over saturated KSCN solution at room temperature to yield 101 grams of clear, amber gel. Analysis of this gel showed it to be a mixture of 84% by weight 2-(trimethylammonio)ethyl dodecylphosphonate, i.e., Compound 7 in Table I hereinbefore, 11% by weight water, and 5% by weight sodium iodide.

2 - (dimethylethylammonio)ethyl dodecylphosphonate can be prepared as above except that an equivalent amount of ethyl iodide is substituted for the methyl iodide above.

EXAMPLE II

Into a 2-liter, stainless-steel autoclave were added 84 grams (0.5 mole) 1-dodecene, 106 grams (1.0 mole) sodium hypophosphite monohydrate, 1 ml. di-tert-butyl peroxide, and 350 ml. methanol. The autoclave was sealed, maintained at 120°C. , and rocked for 17 hours. During this 17-hour period the pressure in the autoclave was 2 atmospheres. After this 17-hour period, the contents of the autoclave were allowed to cool to room temperature, after which the autoclave was opened and the contents removed. The contents were then diluted with 3 liters of distilled water, and then extracted three times, each time with 500 ml. of petroleum ether, and the extracts discarded.

Into the aqueous solution remaining was poured 100 ml. of concentrated hydrochloric acid. During this addition the temperature of the resulting mixture was approximately 35°C. The resulting mixture was extracted three times, each time with 500 ml. of petroleum ether, and the remaining aqueous phase was discarded. These ether extracts were dried over sodium sulfate, and the dried extracts were evaporated on a steam bath under nitrogen to yield 98 grams of crude dodecylphosphonic acid. Recrystallization from 300 ml. of petroleum ether gave 79 grams (0.34 mole) of substantially pure dodecylphosphonic acid.

70 grams (0.3 mole) of this substantially pure dodecylphosphonic acid is then dissolved in 200 ml. diethyl ether at 0°C. To this solution is added a diethyl ether solution of diazomethane prepared by adding 30 grams of N-nitrosomethylurea to a mixture of 75 ml. of 30% aqueous KOH and 250 ml. diethyl ether at $0^\circ\text{--}10^\circ\text{C.}$, and decanting the ether layer from the aqueous layer prior to use. The diazomethane and dodecylphosphonic acid are reacted for 30 minutes at $0^\circ\text{--}10^\circ\text{C.}$ The produced methyl dodecylphosphinate, 74 grams, is isolated by evaporating the diethyl ether and excess diazomethane on a steam bath under nitrogen.

72 grams (0.28 mole) of this methyl dodecylphosphinate is then dissolved in 250 ml. of toluene which has been dried over sodium ribbon. This solution is mixed with 6.5 grams (0.28 mole) sodium dispersed in 250 ml. toluene in a 1-liter, 3-necked, round-bottom flask, equipped with addition funnel, thermometer, reflux condenser protected by a drying tube, and mechanical stirrer. The sodio derivative of the phosphinate is formed by stirring the mixture at $25^\circ\text{C.}\text{--}35^\circ\text{C.}$ for four hours.

The resulting mixture is brought to reflux, i.e., to about 101°C. To this refluxing mixture is added over a three-hour period, 40 grams (0.32 mole) of 2-bromoethanol. After this three hour period, the reaction mixture is allowed to cool to room temperature, after which the precipitated sodium bromide is removed by filtration, and the toluene solvent is removed by vacuum evaporation to yield 82 grams of crude methyl-2-hydroxyethyl-dodecylphosphinate.

This methyl-2-hydroxyethyl-dodecylphosphinate is dis-

solved in 200 ml. of dry petroleum ether contained in a 500 ml. 3-necked flask, equipped with a gas dispersion tube, a drying tube, and a magnetic stirrer. Anhydrous HBr is then passed into the solution for five hours at the rate of 200 cc./min. During the HBr addition the temperature of the mixture rises and levels out at 50°–60° C. After HBr addition, the system is swept with nitrogen for one hour to remove methyl bromide and dissolved HBr. The solvent (petroleum ether and formed water) is evaporated under nitrogen on a steam bath to yield 93 grams of crude 2-bromoethyl dodecylphosphinic acid.

This crude 2-bromoethyl dodecylphosphinic acid is dissolved in 200 ml. acetone. Into this solution is poured 60 grams (1 mole) of trimethylamine. This mixture contained in a 500 ml. boiling flask surmounted with a reflux condenser is refluxed at about 56° C. for 8 hours. The resulting mixture is evaporated on a steam bath. The residue is dissolved in 200 ml. of methanol. This solution is shaken for 30 minutes with a mixture of 0.5 equivalent of cation exchange resin in the hydrogen form and 0.5 equivalent of anion exchange resin in the hydroxide form. The resins are then removed by filtration. The filtrate is evaporated to yield 85 grams of 2-(trimethylammonio)ethyl dodecylphosphinate, i.e., Compound 15 in Table I hereinbefore.

2-(dimethylethylammonio)ethyl dodecylphosphinate and 2-(triethylammonio)ethyl dodecylphosphinate can be prepared as above except that dimethylethylamine and triethylamine, respectively, are substituted for the trimethylamine above.

In another case, 100 grams (0.3 mole) of 2-bromoethyl dodecylphosphinic acid prepared as above is dissolved in 500 ml. of dioxane. To this solution is added 45 grams (0.64 mole) sodium methyl mercaptide. This mixture is maintained at 30° C. for 18 hours. A fast stream of nitrogen is passed through the mixture to remove methyl mercaptan. To the resulting mixture is added 50 grams (0.45 mole) methyl iodide. This reaction mixture is refluxed at about 101° C. for 4 hours. Purification of the refluxed mixture yields 88 grams of 2-(dimethylsulfonio)ethyl dodecylphosphinate, i.e., Compound 16 in Table I hereinbefore.

EXAMPLE III

Into a 1-liter, 3-necked flask, equipped with a thermometer, gas inlet tube, dropping funnel, and mechanical stirring assembly is placed 106 grams (0.69 mole) of POCl₃ and 500 ml. of dry ethylenedichloride. To this formed solution, with stirring, is added dropwise over a 30-minute period 93 grams (0.5 mole) of 1-dodecanol. During this addition, dry nitrogen is passed slowly through the stirred solution. The temperature of the solution starts out at room temperature, i.e., 25° C., and rises about 5° C. during the dodecanol addition. Stirring is continued for 3 hours after addition is completed, during which the temperature of the reaction solution ranges from 25° C. to 30° C. The excess POCl₃ and the ethylenedichloride are then removed by evaporation under water pump vacuum using a 70° C. water bath to speed the evaporation.

The residue from the evaporation, consisting of crude dodecyl dichlorophosphate, is dissolved in 500 ml. of dry ethylene dichloride in apparatus identical with that described in the above paragraph. To this solution is added with stirring over a 45-minute period, 44 grams (0.5 mole) 2-(dimethylamino)ethanol. Stirring is continued for 2 hours after this addition. During the 2-(dimethylamino)ethanol addition period and during the stirring thereafter the temperature of the reaction solution ranges from 25° C. to 30° C. The solvent is then removed by vacuum evaporation.

The residue from this evaporation is dissolved in 500

ml. of methanol containing 40 grams of NaOH and 50 ml. water. This solution is shaken from time to time during a thirty-minute period with a mixture of 1.5 equivalents of cation exchange resin in the hydrogen form and 1.5 equivalents of anion exchange resin in the hydroxide form. The resin is then removed by filtration. The solvent is then evaporated to yield 147 grams of 2-(dimethylammonio)ethyl dodecylphosphate, i.e., Compound 21 in Table I above.

In another case, 100 grams (0.3 mole) of 2-(dimethylammonio)ethyl dodecylphosphate prepared as above is dissolved in 500 ml. of dioxane. To this solution is added over a 10-minute period, 45 grams (0.32 mole) of methyl iodide. The mixture is then brought to reflux temperature, i.e., to about 105° C., and is stirred at this temperature for 30 minutes. To the resulting mixture is added with stirring over a 5-minute period 300 ml. of 1 N NaOH (0.3 mole NaOH). The temperature of the mixture during this addition ranges from 100° C. to 72° C. The resulting mixture is purified by ion exchange to yield 94 grams of 2-(trimethylammonio)ethyl dodecylphosphate, i.e., Compound 2 in Table I hereinbefore.

2-(dimethylethylammonio)ethyl dodecylphosphate can be prepared in the same manner as the 2-(trimethylammonio)ethyl dodecylphosphate above except that an equivalent amount of ethyl iodide is substituted for the methyl iodide above.

Compounds of this invention are useful per se as detergent and surface active agents. Desirably they are used with other materials to form detergent compositions, as for example, liquid, bar, tablet, granular or other compositions. Such detergent compositions can contain the reversed zwitterionics of this invention, and water-soluble inorganic alkaline builder salts, water-soluble organic alkaline sequestrant builder salts or mixtures thereof in a ratio of reversed zwitterionic to builder salt of about 4:1 to about 1:20. Such detergent compositions ordinarily contain from 5% to 50% of detergent active and from 5% to 85% of builder salt.

Granular detergent compositions preferably contain about 5% to about 50% of the reversed zwitterionics of this invention and liquid formulations preferably contain from about 2% to about 30% of such reversed zwitterionics. Granular detergents preferably contain at least an equal amount of an alkaline builder salt. Liquid formulations preferably contain from about 5% to about 40% of a water-soluble alkaline builder salt, the balance of the composition being a solvent such as water, and/or other liquid vehicles. Liquid formulations can also contain a hydrotropic electrolyte, e.g., sodium toluene sulfonate. All percentages and parts herein are by weight unless specified otherwise.

Water-soluble inorganic alkaline builder salts which can be used in this invention alone or in admixture are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates. Ammonium or substituted ammonium, e.g., triethanol ammonium, salts of these materials can also be used. Specific examples of suitable salts are sodium tripolyphosphate, sodium carbonate, sodium tetraborate, sodium and potassium pyrophosphate, sodium and ammonium bicarbonate, potassium tripolyphosphate, sodium hexaphosphate, sodium sesquicarbonate, sodium orthophosphate, and potassium bicarbonate. The preferred inorganic alkaline builders according to this invention are alkali metal tripolyphosphates for built granular and tablet compositions and alkali metal pyrophosphates for built liquid compositions. Potassium is the preferred alkali metal used in liquid compositions and sodium finds best application for granular or tablet compositions.

Examples of suitable organic alkaline sequestrant builder salts used in this invention alone or in admixture are alkali metal, ammonium or substituted ammonium, aminocarboxylates, e.g., sodium and potassium ethylenediaminetetraacetate, sodium and potassium N-(2-hy-

droxyethyl)nitrilodiacetates, sodium and potassium nitrilodiacetates. Mixed salts of these polycarboxylates are also suitable. The alkali metal salts of phytic acid, e.g., sodium phytate are also suitable as organic alkaline sequestrant builder salts (see U.S. Pat. 2,739,942). Also suitable as organic alkaline sequestrant builder salts are the water-soluble salts of polycarboxylate polymers and copolymers as described in the copending application of Francis L. Diehl Ser. No. 269,359, filed Apr. 1, 1963 and now U.S. Pat. 3,308,067 (e.g., polymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid, and citraconic acid and copolymers with themselves and other compatible monomers such as ethylene).

Polyphosphonates are also valuable builders in terms of the present invention, including specifically sodium and potassium salts of ethane-1-hydroxy-1,1-diphosphonic acid, sodium and potassium salts of methylene diphosphonic acid, sodium and potassium salts of ethylene diphosphonic acid, and sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Other examples include the alkali metal salts of ethane-2-carboxy-1,1-diphosphonic acid, hydroxymethanediphosphonic acid, carbonyldiphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, ethane-2-hydroxy-1,1,2-triphosphonic acid, propane-1,1,3,3-tetraphosphonic acid, propane-1,1,2,3-tetraphosphonic acid, and propane-1,2,2,3-tetraphosphonic acid.

Besides the builders being used together with the present reversed zwitterionics, it is also possible according to the present invention to use the reversed zwitterionic compounds of this invention in combination with other cleaning agents such as anionic, nonanionic, and other ampholytic and zwitterionic organic detergent compounds. When it is desired to use such reversed zwitterionic compounds in combination with other detergent compounds, they are preferably utilized with anionic detergents because of the sudsing characteristics of the latter. The ratio of the reversed zwitterionic to such other detergent compound is from about 10:1 to 1:5. If it is desired to use such a reversed zwitterionic in admixture with another detergent compound as the active portion of a cleaning composition, the ratio of such a mixture to the builder salt should be within the previously prescribed range of 4:1 to 1:20. A composition prepared along these lines can contain from 5% to 50% of such a mixture and 5% to 85% of a builder salt selected from water-soluble inorganic alkaline builder salts, water-soluble organic sequestrant builder salts, and mixtures thereof, within the prescribed ratio range.

Examples of anionic soap detergents which can be used in admixture with the reversed zwitterionic detergent, if desired, are the sodium, potassium, ammonium and alkylammonium salts of higher detergent range fatty acids (C_{10} - C_{20}). Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap. Examples of suitable anionic organic non-soap detergents in the form of their water-soluble salts are: alkylglyceryl ethersulfonates; alkyl sulfates; alkyl monoglyceride sulfates or sulfonates; alkylpolyethenoxy ether sulfates; acylsarcosinates; acyl esters of isethionates; N-acyl-N-methyl taurides; alkylbenzenesulfonates wherein the alkyl substituent is straight chain or branched chain; sulfonated alpha-olefins, e.g., such as described in the copending application of Kessler et al., Ser. No. 561,397, filed June 29, 1966; alkylphenol polyethenoxy sulfonates. In these compounds the alkyl and acyl groups, respectively, contain 10 to 24 carbon atoms. They are used in the form of water-soluble salts, the sodium, potassium, ammonium, and alkylammonium salts, for example. Specific examples are: sodium lauryl sulfate, sodium tallow alkyl sulfate; sodium salt of sulfonated alpha-tridecene; potassium N-methyl-N-lauroyl tauride; triethanolammonium tetrapropylbenzene sulfonate; sodium (linear) dodecyl benzene sulfonate.

Examples of nonionic organic detergents which can be used in the compositions of this invention, if desired, are: polyethylene oxide condensates of alkylphenols wherein the alkyl group contains from 8 to 15 carbon atoms (e.g., t-octylphenol) and the ethylene oxide is present in a molar ratio of ethylene oxide to alkylphenol in the range of 8:1 to 20:1; condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine wherein the molecular weight of the condensation products ranges from 5,000 to 11,000; the condensation products of from about 5 to 30 moles of ethylene oxide with one mole of a straight or branched chain aliphatic alcohol containing from 8 to 18 carbon atoms, e.g., condensation product of 6 moles of ethylene oxide with one mole of lauryl alcohol; higher alkyl di-lower alkyl amine or phosphine oxides, e.g., dodecyldimethylamine oxide or dodecyldimethyl phosphine oxide; alkyl methyl sulfoxides such as dodecyl methyl sulfoxide.

Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 10 to about 20 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, phosphinate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, sodium 3-(N-methyl-N-hexadecylamino)-2-hydroxypropane-1-sulfonate and its dodecyl homolog, sodium 3-dodecylaminopropane-1-sulfonate, sodium dodecyl-beta-alanine, sodium N-alkyltaurines such as the one prepared by reacting dodecyl-amine with sodium isethionate according to the teaching of United States Letters Pat. No. 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teachings of United States Letters Pat. No. 2,438,091, and the products sold under the trade name "Miranol" and described in United States Letters Pat. No. 2,528,378.

Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radical may be straight chain or branched, and wherein one of the aliphatic substituents contains from about 10 to about 20 carbon atoms and one contains an anionic water solubilization group, e.g., carboxy, sulfonate, sulfate, phosphate, phosphinate, or phosphonate. Examples of compounds falling within this definition are: 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate and the corresponding dodecyl and tetradecyl homologs and 3-(N,N-dimethyl-N-dodecylammonio)-propane-1-sulfonate and the corresponding hexadecyl and tetradecyl homologs.

It is also possible according to the present invention to use the reversed zwitterionic detergents in combination with anionic brighteners. A detergent composition employing the combination of ingredients ordinarily can contain from about 0.01% by weight to about 2% by weight optical brightener. Examples of anionic optical brighteners which can be used herein are sodium 2-sulfo-4-(2-naphtho-1,2-triazolyl)stilbene and sodium 4,4'-bis(4-anilino-6-morpholino-s-triazo-2-ylamino)-2,2'-stilbene disulfonate.

The detergent compositions of this invention can also contain any of the usual adjuvants, diluents, and additives, for example, perfumes, antitarnishing agents, bacteriostatic agents, dyes, suds builders, suds depressors, and the like, without detracting from the advantageous properties of the composition.

The following examples illustrate detergent compositions containing the reversed zwitterionic compounds of this invention which can be used under conditions of ordinary usage to clean, for example, soiled clothing or dishes. All percentages herein are by weight unless otherwise specified.

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EXAMPLE IV

Solid—granules

	Percent
2-(trimethylammonio)ethyl dodecylphosphonate	17.5
Sodium tripolyphosphate	50.0
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:2.5$)	10.0
Sodium sulfate	17.5
Moisture	5.0

EXAMPLE V

Compressed granules—tablet

2-(trimethylammonio)ethyl dodecylphosphate	31.0
Tetrasodium pyrophosphate	52.0
Trisodium phosphate	10.0
Moisture	7.0

EXAMPLE VI

Solid—granules

	Percent
2-(trimethylammonio)ethyl dodecylphosphinate	32.0
Pentasodium ethane-1-hydroxy-1,1,2-triphosphonate	64.0
Moisture	4.0

EXAMPLE VII

Solid—granules

3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate	20.0
2-(dimethylsulfonio)ethyl dodecylphosphinate	25.0
Sodium tripolyphosphate	35.0
Sodium carbonate	10.0
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:2.5$)	5.0
Moisture	5.0

EXAMPLE VIII

Solid—granules

3-(trimethylammonio)propyl octadecylphosphonate	20.0
Sodium tallow alcohol sulfate	10.0
Trisodium ethane-1-hydroxy-1,1-diphosphonate	20.0
Sodium tripolyphosphate	10.0
Sodium nitrilotriacetate	10.0
Sodium sulfate	8.0
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:2.5$)	11.0
Moisture	11.0

EXAMPLE IX

Liquid

2-(dimethylsulfonio)ethyl decylphosphonate	5.0
Sodium salt of SO_3 sulfonated 1:1 weight mixture of alpha-dodecene and alpha-tetradecene	10.0
Tetrapotassium pyrophosphate	19.0
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:1.6$)	3.8
Potassium toluene sulfonate	8.5
Carboxymethyl hydroxyethyl cellulose	.3
Water, balance.	

EXAMPLE X

Liquid

2-(diethylsulfonio)ethyl decylphosphate	6.0
Sodium (linear) dodecyl benzene sulfonate	6.0
Tetrapotassium propane-1,1,3,3-tetraphosphonate	20.0
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:1.6$)	3.8
Potassium toluene sulfonate	8.5
Carboxymethyl hydroxymethyl cellulose	.3
Water, balance.	

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EXAMPLE XI

Solid—granules

2-(dimethylammonio)ethyl dodecylphosphonate	5.0
Condensation product of 10 moles of ethylene oxide and one mole of tallow fatty alcohol	5.0
Sodium (linear) tridecyl benzene sulfonate	10.0
Dodecylmethyl phosphine oxide	5.0
Coconut oil soap	5.0
Sodium tripolyphosphate	50.0
Tetrasodium ethylene diamine tetraacetate	20.0

EXAMPLE XII

Solid—granules

Potassium dichloroisocyanurate	11.43
Sodium tallow fatty alcohol sulfate	11.0
2-(trimethylammonio)ethyl dodecylphosphonate	5.0
Sodium tripolyphosphate	40.0
Trisodium phosphate	23.5
Sodium carboxymethylcellulose	0.36
Sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 1.6:1)	6.0
Perfume	0.25
Sodium 2-sulfo-4-(2-naphtho-1,2-triazolyl)stilbene	0.1
Moisture, balance.	

It will be appreciated that the reversed zwitterionic compounds used in the present invention can be incorporated into many other liquid or granular detergent compositions with suitable adjustments being made in the other components.

Materials which are considered normal and desirable additives in liquid or granule detergent compositions can be added to the compositions of this invention without adversely affecting or modifying basic cleaning characteristics. For example, a tarnish inhibitor such as benzotriazole or ethylene thiourea may be added in amounts up to about 1%. Fluorescers, perfume, bleaching agents, color, antiredeposition agents, antibacterial agents, thickening agents, opacifiers, and blending or viscosity control agents, while not essential in the compositions of this invention, may also be added.

The compositions of the present invention can be used in conjunction with cool water washing situations as well as with warm and hot water.

What is claimed herein is:

1. A detergent composition consisting essentially of a reversed zwitterionic phosphorus compound having the formula $\text{R}-\text{Z}-\text{R}^1-\text{X}$ wherein R is selected from alkyl and alkenyl of from about 10 to about 20 carbon atoms; Z is a negatively charged radical selected from the group consisting of phosphate, phosphonate, and phosphinate radicals; R^1 is an alkylene radical containing from 2 to about 4 carbon atoms; and X is a positively charged radical selected from the group consisting of ammonium and tertiary sulfonium radicals; said ammonium radical having the formula



wherein R^2 , R^3 and R^4 are each selected from the group consisting of hydrogen, methyl, and ethyl; said tertiary sulfonium radical having the formula



wherein R^5 and R^6 are each selected from the group consisting of methyl and ethyl; and a builder selected from the group consisting of water-soluble inorganic builder salts, water-soluble organic alkaline sequestrant builder salts and mixtures thereof, the weight ratio of said reversed zwitterionic phosphorus compound to said builder being in the range of about 4:1 to about 1:20.

2. The detergent composition of claim 1 wherein the reversed zwitterionic phosphorus compound is 2-(trimethylammonio)ethyl dodecylphosphonate.

3. The detergent composition of claim 1 wherein the

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reversed zwitterionic phosphorus compound is 2-(dimethylammonio)ethyl dodecylphosphonate.

4. A built detergent composition consisting essentially of about 5% to about 50% of a mixture of a reversed zwitterionic phosphorus compound having the formula $R-Z-R^1-X$ wherein R is selected from alkyl and alkenyl of from about 10 to about 20 carbon atoms; Z is a negatively charged radical selected from the group consisting of phosphate, phosphonate, and phosphinate radicals; R^1 is an alkylene radical containing from 2 to about 4 carbon atoms; and X is a positively charged radical selected from the group consisting of ammonium and tertiary sulfonium radicals; said ammonium radical having the formula



wherein R^2 , R^3 and R^4 are each selected from the group consisting of hydrogen, methyl, and ethyl; and an organic

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anionic detergent; the ratio of the reversed zwitterionic detergent compound to said organic anionic detergent being in the range of 10:1 to 1:5 and from 5% to 85% of a builder material selected from the group consisting of water-soluble inorganic alkaline builder salts; water-soluble organic alkaline sequestrant builder salts; and mixtures thereof.

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