United States Patent Office 3,749,675 Patented July 31, 1973

3,749,675

PHOSPHATE-FREE DETERGENTS

Edward H. Chang, Burnsville, Minn., assignor to Fremont Industries, Inc., Shakopee, Minn.

No Drawing. Filed Nov. 12, 1970, Ser. No. 89,146
Int. Cl. C11d 1/72, 3/00, 3/08
U.S. Cl. 252—135 1 Claim

ABSTRACT OF THE DISCLOSURE

A phosphate-free general purpose laundry detergent based substantially upon the sodium salt of citric acid and containing a builder substance, the builder substance being a polyalkylene glycol ether which is the reactant product of a hydrophobic reactant and a hydrophilic reactant. The combination of the substances provides an optimized general purpose laundry detergent.

CROSS-REFERENCE TO RELATED APPLICATION

The present invention is a modification of that invention disclosed and claimed in U.S. patent application Ser. No. 44,535, filed June 8, 1970, entitled "Detergent Composition" in which the present inventor is named as a co-inventor, and which application is assigned to the assignee of the present invention.

BACKGROUND OF THE INVENTION

In the past, it has been traditional to utilize general purpose detergent compositions based upon condensed inorganic polyphosphate compounds such as alkali metal tripolyphosphates and higher condensed phosphates. These phosphate compositions which constitute the most widely commercially used builders for detergent compositions, have a strong tendency to hydrolyze into less condensed phosphorous compounds which are relatively inferior builders, and which may form undesirable precipitates in washing solutions.

Detergents based upon phosphates have contributed significantly to aquatic plant growth. In standing bodies of water, weed growth is normally inhibited because of the lack of available phosphorus. However, when quantities of waste detergents and the like, containing substantial quantities of phosphorus in the form of phosphates and the like, are discharged into such bodies of water, weed growth is encouraged and may proceed on a substantially unchecked basis. Over-abundant weed and plant growth in such bodies of water contributes substantially to the oxygen demand of the body of water, and hence is a well recognized source of pollution in bodies of water.

The present invention provides a general purpose laundry detergent which is free of phosphorus, and hence is desirable for most normal water and waste disposal systems.

The composition of the present invention provides a phosphate-free detergent containing sodium citrate and comprising a polyalkylene glycol ether surfactant with a hydrophobic and a hydrophilic portion. The composition provides a system with a balanced level of ingredients, the balanced level of ingredients contributing to a synergistic operating effect in the overall composition.

In the past, various attempts have been made to provide phosphate-free compositions for use as general purpose laundry detergents or the like, however, these attempts have normally been unsuccessful because of the inferior cleaning capability of the compositions. Because of this recognized inferior performance, those laundry detergent compositions in use today have traditionally utilized phosphates.

SUMMARY OF THE INVENTION

Briefly, in accordance with the present invention, a general purpose laundry detergent is provided based upon the sodium salt of citric acid and containing a polyalkylene glycol ether surfactant with hydrophobic and hydrophilic portions. The hydrophobic portion comprises an aliphatic monohydric alcohol containing from one to eight carbon atoms to which is attached a heteric chain of oxyethylene and oxypropylene. The oxypropylene portion of the heteric chain ranges from between about 85 percent and 90 percent of the total chain, the molecular weight of the hydrophobic portion being from between about 1000 and 2000. The hydrophilic portion comprises a polyoxyethylene chain, with the hydrophilic portion comprising between about 44 percent and 55 percent of the total molecular weight of the product. The molecular weight of the polyalkylene glycol ether utilized in connection with the present invention preferably ranges from between about 2500 and 3500.

In addition, the compositions of the present invention contain surface active agents, components to control the pH of the material and its working solutions, and may also contain, if desired, brighteners, dyes, perfumes or odorants.

Therefore, it is a primary object of the present invention to provide a general purpose laundry detergent which is free of phosphorus or phosphate constituents, and which is based substantially upon the sodium salt of citric acid containing a builder substance of a polyalkylene ether with both hydrophobic and hydrophilic portions.

It is yet a further object of the present invention to provide such a general purpose laundry detergent wherein the composition comprises sodium citrate and wherein the composition contains a surfactant which comprises a hydrophobic portion comprising an aliphatic monohydric alcohol containing from one to eight carbon atoms to which is attached a heteric chain of oxyethylene and oxypropylene, and wherein the hydrophilic portion comprises a polyoxyethylene chain.

Other and further objects of the present invention will become apparent to those skilled in the art upon a study of the following specification and claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to better appreciate the aspects of the present invention, a preferred general purpose laundry detergent in accordance with the present invention is set forth hereinbelow:

Example I

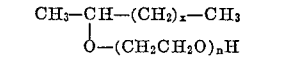
Component:	Percent by weight
Nonionic surface active agent	7
Sodium citrate ($C_6H_5Na_3O_7$)	15
Polymeric organic surfactant substance	6
Sodium silicate solids (Na_2O:SiO_2 between about 0.46 and 1.0)	12
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	17
Sodium carbonate	27
Sodium carboxymethylcellulose	1.5
Brighteners, dye, perfume and water	To 100

The nonionic surface active agent which is employed in the compositions of the present invention is selected from the group consisting of the ethylene oxide adduct of linear primary and linear secondary alcohols, as well as the ethylene oxide adduct of alkylphenols. Such surface active agents are commencially available, and may be characterized by the following structural formulas:

$$CH_3—(CH_2—)_xCH_2—(OCH_2CH_2—)_nOH$$

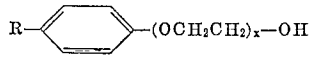
wherein "x" is an integer having an average value of be-

tween about 6 and 20, and wherein "*n*" is an integer having an average value of between about 5 and 12. In connection with linear secondary alcohols, a composition having the following structural formula may be utilized:



wherein "*x*" is an integer having an average value of between about 8 and 14, and wherein "*n*" is an integer having an average value ranging from between about 7 and 12.

When the ethylene oxide adduct of alkylphenols is utilized, the composition having the following structural formula may be utilized:



wherein "R" is an alkyl radical containing from between about 8 and 9 carbon atoms, and wherein "*x*" is an integer having an average value ranging from between about 7 and 13. Surface active agents of the above identified compositions are, of course, commercially available.

The sodium salt of citric acid is utilized as one of the primary constituents of the detergent composition of the present invention. This material is, of course, commercially available.

In combination with this sodium salt of citric acid, a polymeric organic surfactant compound is employed, this compound being a polyalkylene glycol ether containing hydrophobic and hydrophilic portions. These compositions are generally described as heteric-block polymers containing ethylene oxide and propylene oxide, and having molecular weight in the range of between about 2500 and 3500. These heteric-block nonionic surfactants contain a hydrophobic and a hydrophilic portion or component. The hydrophobic portion generally has a minimum molecular weight in the range of about 1000, and consists of an aliphatic monohydric alcohol containing from one to about eight carbon atoms, this monohydric alcohol having attached thereto a heteric chain of oxyethylene and oxypropylene. The weight ratio of oxypropylene to oxyethylene is preferably between about 95:5 and 85:15. The hydrophilic portion is attached to the hydrophobic portion, and contains a polyoxyethylene chain comprising between about 44.4 percent and 54.6 percent of the total molecular weight of the surfactant composition.

These products, which are commercially available, are normally made in a two-step process. In the first step or operation, the ethylene oxide and propylene oxide components are brought into intimate contact with a monofunctional initiator in liquid phase, a catalyst being uniformly distributed. This process is defined in detail in U.S. Pat. No. 3,078,315. In the second operation, ethylene oxide is added under normal conditions of oxyethylation. Following completion of the reaction, the reactant product is removed from the reaction vessel and neutralized, with impurities being removed by extraction with organic solvents and stripping.

Maximum detergency is normally obtained with the hydrophobic portion having an average molecular weight of between about 1200 and 1500, and while higher molecular weights can be utilized, it has been found that increasing the molecular weight of about 2000 produces little, if any, improvement in detergency. Maximum detergency has also been found with a weight ratio of ethylene oxide adduct to hydrophobic component of about 1:1.

Sodium silicate is preferably employed with the ratio of $Na_2O:SiO_2$ ranging from between about 0.46 and 1. These compositions are, of course, commercially available.

As a modified composition, utilizing the aspects of the present invention, the following range of formulation may be employed:

TABLE I

Component:	Useful range percent by weight
Nonionic surface active agent	5–15
Sodium citrate ($C_6H_5Na_3O_7$)	5–30
Polymeric organic surfactant substance (polyalkylene glycol ether)	3–15
Sodium silicate ($Na_2O:SiO_2$ between about 0.46 and 1.0)	3–20
Borax	5–25
Sodium carbonate	15–30
Sodium carboxymethylcellulose	0.5–1.5
Brightener, dye, perfume and water	To 100

The sodium carboxymethylcellulose is preferably utilized in a two percent solution in water, and ideally has a viscosity at 25° C. of between about 30 and 105 centipoises.

The use of brighteners, dyes and perfumes is universally practiced in the detergent industry. The brighteners utilized are commercially available brighteners which are normally employed in detergent compositions for synthetic fibers. Their use, while not critical to the detergent composition of the present invention, is nevertheless desirable in most instances for achieving a product which may be utilized for a wide variety of home laundry purposes.

In order to illustrate the effectiveness of the compositions of the present invention, the compositions set forth in Example I hereinabove were utilized on a comparative basis with a commercially available laundry detergent utilizing a substantial quantity of sodium tripolyphosphate with the results being tabulated hereinbelow. The commercially available detergent composition based upon phosphate had the formulation identified as follows:

PHOSPHATE-BASED LAUNDRY DETERGENT

Component:	Percent by weight
Sodium tripolyphosphate	40
Sodium silicate	12
Nonionic surface active agent	7
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	17
Sodium carbonate	22
Sodium carboxymethylcellulose	1.5
Brighteners, dye, perfume and water	To 100

The test conditions were as follows:

TEST CONDITIONS

Detergent concentration used	0.2%
Water hardness as $CaCO_3$	300 p.p.m.
Time:	
Wash cycle	15 minutes.
Rinse cycle	5 minutes.
Test machine	Terg-O-Tometer.
Agitator speed	125 r.p.m.
Temperature	120° F.
Test cloth:	
Cotton, soiled	U.S. Testing, Inc.
Cotton, wash wear, soiled	Test Fabrics, Inc.
Dacron, soiled	Do.
Dacron/cotton, perma press finish, soiled	Do.
Reflectance meter	Photovolt reflectometer.

The test results obtained are as follows:

PERCENTAGE SOIL REMOVAL

Product	Phosphate base	Composition of Ex. I
Test cloth:		
Cotton, soiled	46	48
Cotton, wash wear soiled	56	60
Dacron, soiled	26	30
Dacron/cotton perma press, soiled	42	46
Total	170	184

It will be appreciated that the compositions of the present invention provide an ideal general purpose laundry detergent having cleaning capabilities which are at least equivalent to those of the heavily phosphate type. They are ideally suited for use in home laundry operations, wherein the cleaning water is frequently discharged into municipal sewage systems or into private septic or disposal systems utilizing subterranean water drainage.

I claim:

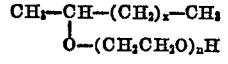
1. A cleaning composition having the following composition:

Component:	Percentage by weight
Nonionic surface active agent	7
Sodium citrate (trisodium salt)	15
Polymeric organic surfactant compound (polyalkylene glycol ether)	6
Sodium silicate (Na_2O:SiO_2 between about 0.46 and 1.0)	12
Borax	17
Sodium carbonate	27
Sodium carboxymethylcellulose	1.5
Brighteners, dye, perfume and water	To 100

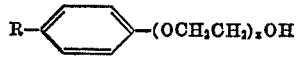
wherein the nonionic surface active agent is selected from the group consisting of the ethylene oxide adduct of linear primary alcohols, linear secondary alcohols, and alkylphenols, said ethylene oxide adducts having the following structural formulas:

$$CH_3—(CH_2—)_xCH_2—(OCH_2CH_2—)_nOH$$

wherein "x" represents an integer having an average value from between about 6 and 20, and wherein "n" is an integer having an average value of between about 5 and 12;



wherein "x" is an integer having an average value of between about 8 and 14, and wherein "n" is an integer having an average value between about 7 and 12;



wherein "R" is an alkyl chain having from between about 8 and 9 carbon atoms, and wherein "x" is an integer having an average value of between about 7 and 13;

said polymeric organic surfactant compound being a polyalkylene glycol ether consisting essentially of a hydrophobic reactant and a hydrophilic reactant forming a reactant product with a molecular weight ranging from between about 2500 and 3500, the hydrophobic reactant being an aliphatic monohydric alcohol containing from 1 to 8 carbon atoms to which is attached a heteric chain of oxyethylene and oxypropylene, with the oxypropylene portion of the heteric chain ranging from between 85 percent and 95 percent of the total chain, and wherein the hydrophilic reactant is a poly-oxyethylene chain comprising from about 44 percent and 55 percent of the total molecular weight of the product.

References Cited

UNITED STATES PATENTS

3,459,670	8/1969	Carter	252—99
3,368,978	2/1968	Irani	252—137
3,308,067	3/1967	Diehl	252—161
3,078,315	2/1963	Steele et al.	252—89 X
2,264,103	11/1941	Tucker	252—132 X

OTHER REFERENCES

"Tergitol Surfactants," bulletin of Union Carbide Co., 1961, pp. 1–5, 12, 28 and 29.

"Phosphate Replacements: Problems With the Washday Miracle," by Allen L. Hammond, Science, vol. 172, pp. 361–363.

"Ecologic Detergents: Will the Bubble Burst?," article in Chemical Week, Apr. 28, 1971, pp. 10–12.

"Hazard Cited in 'Cleaner' Detergents," by Nancy L. Ross, The Washington Post, Sept. 16, 1971.

LEON D. ROSDOL, Primary Examiner

D. L. ALBRECHT, Assistant Examiner

U.S. Cl. X.R.

252—89, 132, Dig. 1