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DETERGENT COMPOSITIONS CONTAINING SILICA COLLOIDS

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ABSTRACT OF THE DISCLOSURE

This invention is concerned with detergent compositions containing colloidal silica to enhance their cleaning and soil removal ability. The colloidal silica is formed in situ as a sol by the reaction of water-soluble or dispersible alkali silicates with a variety of anionic, detergent-forming organic acids, exemplified by fatty acids of from eight to twelve carbon atoms or alkyl aryl sulfonic acids. The colloidal silica is characterized by an alkaline oxide to SiO_2 ratio of from 1:4 to 1:2000 or more.

BACKGROUND OF THE INVENTION

The present invention is directed to improving the cleaning and soil removing ability of detergent compositions, while simultaneously permitting the elimination of certain previously used components which are frequently considered detrimental when present in cleaning composition effluent.

It has been discovered that the soil removal ability of detergent compositions and the prevention of redeposition of soil from such compositions after removal is markedly improved by forming colloidal silica sols in situ with the detergent. The presence of the colloidal silica in detergent compositions among other advantages eliminates the need for including phosphates, which have been found to have a deleterious effect on plant and marine life when included in detergent wastes discharged into bodies of fresh water.

Alkali silicates, such as lithium, sodium and potassium crystalline and soluble amorphous silicates have been used as a component of cleaning compositions for many years. Frequently such compounds are referred to as "builders." Alkali silicates are of particular interest as components of detergent compositions in view of their corrosion inhibiting properties and their buffering characteristics, permitting the maintenance of a substantially constant pH until nearly depleted. Further, when such silicates are employed as a component of a cleaning composition, they provide alkalinity for activation of oil type soils, influence the soil-liquid interface to assist in detachment of soil from substrates, assist in the deflocculation of soils and prevent the redeposition of detached and deflocculated soils. However, the use of such silicates has been largely confined to compositions wherein the pH is in excess of 11.2 in order to maintain the crystalline silicate in molecular or ionic form or the soluble amorphous silicate in an active form.

Heretofore "built" soap has been made by dissolving a commercial liquid silicate, having an approximate ratio of alkali oxide to silicon dioxide of 1:3.22, in kettle soap at 180° F., in an amount equal to about six percent of the soap on an anhydrous basis. The most prominent silicates used as components in detergent compositions are the sodium silicates.

The silicates are frequently referred to or characterized by their alkaline oxide to silica ratio, such as their ratio of Na_2O to SiO_2 . Orthosilicate, having the formula Na_2SiO_4 , is the most alkaline having a Na_2O to SiO_2 ratio of 2:1. Metasilicate, Na_2SiO_3 , has a Na_2O to SiO_2 ratio

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of 1:1. The so-called "water glass" silicates, which are soluble in water, have a Na_2O to SiO_2 ratio in the range of about 1:1.5 to 1:3.8.

Colloidal silica is normally difficultly soluble or dispersible in water or aqueous solutions of alkali fatty acid soaps or organic non-soap detergents. However, as a result of the present discovery, it is now possible to incorporate colloidal silica with such detergent compositions. When so incorporated, the colloidal silica exhibits a profound and surprising influence on the soil removing ability of the detergents.

The colloidal silica contemplated herein is formed in situ as a sol by the reaction of water-soluble or dispersible alkali silicates with detergent-forming organic acids, such as soap-forming fatty acids containing from 8 to 22 carbon atoms in the carbon chain or organic acids which are capable of forming water-soluble non-soap detergents upon neutralization with alkali such as sodium or potassium hydroxide. Due to the fact that the colloidal alkali silicate particles resulting from the present invention are, for the most part, composed predominately of silica (SiO_2), the colloidal particles are, at times, referred to herein as colloidal silica.

It has been found that alkali silicates can be reacted with the aforementioned organic acids, in the manner disclosed herein, forming colloidal silica sols, which are stable within a pH range of 7.2 to 11.0. Further, the sols are also stable at levels of silica (SiO_2) as high as seven percent or more by weight based on the total weight of the detergent composition. On an anhydrous basis, the colloidal silica will generally comprise between about 5 to 25 percent by weight of the non-water components. The reaction between the alkali silicate and the organic acid is considered to comprise a double decomposition involving a partial removal of alkali ions from the soluble alkali silicate. These alkali ions are then bound up with the anion portion of the organic acid to form the alkali salt of the acid. A colloidal silica sol is simultaneously formed in situ wherein the colloidal silica has a reduced alkaline oxide content and an increased SiO_2 content. More particularly, the silica particles have an alkaline oxide to SiO_2 ratio within the range of about 1:4 to 1:2000 or more. The colloidal silica particles are believed, for the most part, to be polymeric in form.

As indicated above, alkali silicates are generally defined in terms of their alkaline oxide to SiO_2 ratio rather than by formula. Various alkali silicates may be used in making the colloidal silica sols contemplated, provided they are readily soluble or dispersible in water. Examples of silicates which may be used for purposes of this invention are sodium silicate ($\text{Na}_2\text{O}-\text{SiO}_2$, ratio of 1:3.22), sodium ortho silicate ($\text{Na}_2\text{O}-\text{SiO}_2$, ratio of 2:1) and potassium silicate ($\text{K}_2\text{O}-\text{SiO}_2$, ratio of 1:2.50).

The organic acids to be reacted with the alkali silicates within the scope of this invention may be classified generally as anionic, detergent-forming acids. Illustrative of such acids are: saturated or unsaturated fatty acids, having a carbon chain containing from about 8 to 22 carbon atoms, exemplified by lauric, stearyl, oleic and linoleic acid; alkyl aryl sulfonic acids, wherein the alkyl group (both linear and branched) has a carbon chain of at least four carbon atoms, and preferably, from 10 to 12 carbon atoms in the chain, exemplified by dodecyl benzene sulfonic acid and nonyl benzene sulfonic acid; alkyl phenol polyethenoxy sulfonic acids; alkyl sulfuric acid such as dodecyl sulfuric; alkyl alkoxy sulfuric acids; petroleum or naphthenic acids and the rosin acids. Due to factors such as cost, availability, stability of the colloid-containing compositions and required characteristics of the end product, the presently preferred acids are the fatty acids and the alkyl benzene sulfonic acids and, particularly,

such benzene sulfonic acids which are characterized by a substantially linear alkyl chain and are biodegradeable.

In preparing detergent compositions containing the colloidal silica sols of the present invention, either a batch or continuous process may be employed. Initial reactants are used in amounts which will result in concentrations, preferably, of between about 10-35 percent by weight. The concentrated product may then be diluted by the addition of water for use generally within the range of about 1:100 to 1:500 parts by weight, depending upon the application. In order to insure the formation of the desired colloidal silica sol, the reaction should be conducted so as to yield a composition with an alkali ion concentration no higher than 0.2 Normal.

The alkali silicate and anionic, detergent-forming acid in desired concentrations, approximately stoichiometric proportions or slight excess of silicate, normally, are

The alkali silicate and anionic, detergent-forming acid in desired concentrations, approximately stoichiometric proportions or slight excess of silicate, normally, are heated separately prior to mixing to a temperature within the range of about 120° F. to 160° F. and preferably to about 140° F. While lower temperatures may be used, the rate of the reaction can be expected to decline. If higher temperatures are employed, the reaction products will tend to form gels. After the preliminary heating, the reactants are normally introduced simultaneously into a reaction vessel or chamber at or substantially at atmospheric pressure. Generally the vessel should be closed to prevent "skinning" of the alkali silicate due to evaporation and the reaction mass subjected to agitation. After the reaction has been completed, usually in about thirty minutes, the pH is adjusted to the desired level by the addition of the acid or silicate, depending upon the pH of the reaction mass and the required pH. The composition is permitted to cool to about room temperature and is then subjected to multiple passes through a colloid mill. The initial pass is preferably made with a rotor-stator setting of about 0.035 inch with the final pass being made at a rotor-stator setting of approximately 0.004 inch. The colloidal particles of the final product should be less than 5 microns. In lieu of a colloid mill, a homo mixing-shearing device may be used, such as Dispersator manufactured by the Premier Mill Corporation.

In producing the stable silica sol detergent compositions by a continuous process, a sodium silicate solution and the organic acid, such as linear dodecyl benzene sulfonic acid, are preferably heated to about 140° F. in separate vessels and then continuously metered in substantially stoichiometric proportions by means of positive displacement metering pumps into a steam jacketed horizontal cylindrical reactor. By way of illustration, a jacketed reactor of about ten feet in length and having a diameter of about twice the diameter of the outlet of the two metering pumps may be used. The reactor is connected to the inlet of a double impeller pump, such as a Bump pump, designed to pump hot slurries. The output of the impeller pump is regulated to equal that of the two metering pumps, which, in a current embodiment, has been established at approximately 30 gal./min. The outlet of the Bump pump is connected to another jacketed horizontal cylindrical receiver of about ten feet in length, wherein the temperature is held at about 140° F. To the end of this receiver there is connected by means of expansion joints a 180° bend which, in turn, is connected to a 50 foot length of pipe jacketed for cooling. The cooling pipe discharges into a surge tank which, in turn, discharges into a colloid mill operating with an 0.035 inch gap between the rotor stator. The mill discharges into a second colloid mill which operates with a rotor-stator clearance of 0.004 inch.

The pH of the final product should be adjusted to within the range of 7.2 to 11.0, with the specific pH depending upon the composition and contemplated end

use. If the pH is permitted to rise above 11.0, the system will tend to form unstable gels or depolymerize to ionic silicate or, in some instances, the colloidal particles will agglomerate, thereby reducing their soil adsorption ability. When the pH is permitted to fall below 7.2, the colloidal silica particles will aggregate to insoluble silica masses. Accordingly, it is an important feature of this invention that compositions containing colloidal silica as contemplated be maintained within the aforementioned pH range to prevent impairment of the enhanced soil removal and adsorption ability of the colloidal silica.

The colloidal silica sol-detergent compositions may be used as made for various soil removal tasks such as personal cleaning, laundering, metal cleaning and general maintenance and hard surface cleaning in institutions, industrial plants and transportation equipment. Alternately, solid compositions may be formed, such as by spray drying. The compositions may be employed in wipe-on wipe-off methods or in tank immersion methods. Detergent compositions containing the colloidal silica have been found to exhibit excellent corrosion resistant behavior when used to clean metals and, particularly, sensitive metals such as aluminum and zinc.

Various auxiliary agents may be incorporated and blended with the colloidal silica sol-detergent compositions such as optical brighteners, illustrated by diamino stilbene or diamino-dibenzofuran, dispersing or suspending agents such as dinaphthalene methane sodium sulfonate, anti-redeposition agents, illustrated by sodium carboxy methyl cellulose, auxiliary organic detergents such as nonylphenolpolyoxyethylene ethanol, lauryl amide, special agents such as polystyrene sodium sulfonate, and ion control or chelating agents such as ethylene diamine sodium tetraacetate.

It is important, however, that the inclusion of water soluble alkali builders, illustrated by sodium or potassium orthophosphates, or complex phosphates, alkali carbonates, borates, silicates or neutral salts such as sodium chloride, sodium sulfate or magnesium sulfate be restricted to levels of concentration of the order of 4.0% by weight or lower. Otherwise, the desired advantages of the colloidal silica on the removal of sols will be found to be appreciably impaired.

An important feature of the present invention resides in the influence of the colloidal silica on waste disposal systems and bodies of water into which the effluent of cleaning systems are discharged. Detergent compositions that are currently employed for household and industrial cleaning frequently incorporate up to fifty percent or more of phosphates in the form of complex and/or ortho phosphates. Such phosphates generally are not removable by presently employed waste water treatment methods and, accordingly, are discharged in large amounts into bodies of fresh surface waters such as lakes and rivers. These phosphate compounds function as nutriment in the water and, accordingly, accelerate and increase the growth of algae and other lower forms of plant life. Excessive algae growth creates an unfavorable biochemical oxidation demand in the water and adversely affects the normal environment of other forms of marine life, including fish. The algae go through a growth cycle and die. The dead decaying algae liberate toxins that have been found detrimental to fish.

It is estimated from data of water resources census that the majority of the phosphates entering many fresh water supplies originate in detergent compositions. The other importation source of phosphates is apparently agricultural fertilizer. Home laundry detergents constitute the major source of phosphates introduced into fresh water supplies.

Heretofore the use of complex phosphates, particularly in the form of sodium tri-polyphosphate, was essential for obtaining adequate cleansing results when fabrics were washed with organic non-soap detergent such as alkyl-

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benzene sodium sulfonate. In the absence of sodium tripolyphosphate soil removal from cottons is inadequate and soil redeposition is rampant.

Certain substitutes for sodium tripolyphosphate have been proposed, such as trisodium nitrilo triacetate, ethylene diamine tetraacetic acid sodium salt and sodium citrate. All of these proposed replacements are more costly to use than sodium tripolyphosphate. Their use, however, poses other problems. All function by chelating cations of hard water, calcium and magnesium. In addition to chelating calcium and magnesium, however, they also chelate heavy metal cations such as iron, lead, copper, aluminum and zinc. These chelating compounds and chelated heavy metal cations are not removed in treatment of waste water and are discharged into fresh water supplies where they can accumulate and eventually disqualify the fresh water as a supply of potable water. Also the influence of accumulated chelating chemicals on human and domestic animal physiological well-being is not now known.

Trisodium nitrilo triacetate is also capable of functioning as an aquatic plant nutrient and, accordingly, can contribute to the eutrophication of fresh water supplies.

Detergent compositions containing colloidal silica of the instant invention do not embody any of the deleterious properties of the compositions containing phosphates and/or chelating agents such as nitrilo triacetate ethylene diamine tetraacetic acid or citric acid as water soluble salts. Such silica sols are inert and do not influence the efficiency of waste disposal treatments. Thus, they have no influence on marine life, either plant or fish life. Accordingly, colloidal silica of the type disclosed herein are preferred substitutes for phosphates or chelating compounds in detergent compositions, providing adequate soil removal and adequate prevention of redeposition of soil without adversely affecting fresh water supplies, or the use of the water supplies.

By way of further illustrating the principles of the present invention, the following examples are disclosed.

EXAMPLE I

One thousand fifty (1050) pounds of sodium silicate having a Na_2O to SiO_2 ratio of 1:3.22 and correspondingly an Na_2O content of 8.90% and an SiO_2 content of 28.7% are diluted with three thousand (3000) pounds of water to form a solution and heated in a jacketed vessel to a temperature of 140° F. A closed vessel is used to prevent "skinning" of the sodium silicate solution by surface evaporation. In a separate mixing vessel seven hundred and ten (710) pounds of linear dodecyl benzene sulfonic acid are heated to 140° F.

The preheated dodecyl benzene sulfonic acid is pumped to a reaction vessel provided with a turbine blade agitator. With the temperature held at 140° F. and the agitator rotating at 60 r.p.m., the preheated sodium silicate solution is metered to the reaction vessel. A double decomposition reaction takes place with the formation of the sodium salt of dodecyl benzene sulfonic acid and a colloidal silica sol. After the reaction has gone to completion, in the order of 30 minutes, the pH of the concentrated colloidal silica sol is adjusted to a level of 10.8. Approximately six percent by weight of the product is the colloidal silicate. The reaction mass is allowed to cool to 75° F. and is then subjected to multiple passes through a colloid mill. The initial clearance of the rotor-stator is set at 0.035 inch to break up coarse agglomerates. After one pass the rotor-stator clearance is adjusted to 0.004 inch and the entire reaction mass is remilled to break up small agglomerates.

The colloidal silica particles exhibit an $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of from 1:4 to the order of 1:2000 or higher and have diameters of less than 5 microns. When one part of the concentrated reaction product, having a pH of 10.8, is diluted to 500 parts with water, the pH of the dispersion is lowered to 9.7. Only traces of ionic silica or active silica are present. When various dilutions of the colloidal

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silica sol ranging from the concentrate to 1:500 parts of water are acidulated and treated with a 10% solution of ammonium molybdate the amount of active silica found, as shown by the presence of the yellow compound:



is estimated as a trace throughout the entire range of dilutions from the concentrate to 1:500.

EXAMPLE II

Nine hundred (900) pounds of nonylphenoltetrapolyoxyethylene ethanol acid sulfate are heated to a temperature of 140° F. In a separate closed vessel, one hundred and twenty (120) pounds of an aqueous solution of potassium silicate, consisting of 3% K_2O and 7.5% SiO_2 , are diluted with two thousand (2000) pounds of water heated to 140° F. The two solutions are pumped simultaneously at a rate of 10 gal./min. into a third closed vessel which is fitted with a turbine type agitator. The agitator is operated at 60 r.p.m. and the mass is held at 140° F. for 30 minutes under constant agitation.

A double decomposition reaction takes place, resulting in the formation of the potassium sulfuric ester of nonylphenoltetrapolyoxyethylene ethanol, an organic non-soap detergent, and a stabilized colloidal silica sol, which has been determined to be essentially polymerized colloidal silica particles with only a trace amount of ionic or active silica present.

The pH of the reaction mixture is adjusted to 10.8 by the addition of the polyoxyethylene acid sulfate if the pH is high and aqueous potassium silicate solution if the pH is below the optimum level of 10.8.

The composition is allowed to cool to 75° F. and is then passed through a colloid mill with an initial rotor-stator clearance of 0.035 inch. As the composition is recirculated through the colloid mill, the rotor-stator clearance is gradually reduced to 0.004 inch. Finally the entire composition is passed through the mill at this clearance.

The colloidal silica sol-organic detergent mixture may be used as is at elevated or ambient temperatures or diluted with water for personal cleansing, cleaning soft goods such as soiled cotton clothes or textiles, cleaning hard surfaces such as dishes, table ware, cooking utensils or industrial metal parts fabricated from steel, aluminum, copper, brass or zinc. Corrosion behavior of the composition is excellent even at levels of dilution up to 1:500 with distilled water. Known detergent additives, except alkali salts, acid and neutral salts, can be employed with the composition where advantageous.

EXAMPLE III

A soap composition embodying a colloidal silica sol can be made in either bar, spray-dried or powder form.

Three thousand (3000) pounds of a mixture of the fatty acids of tallow and coconut oil, in the proportion of 80 weight percent tallow fatty acid and 20 weight percent coconut oily fatty acid, are charged to a jacketed soap crutcher. The mixture is heated to a temperature of 160° F. In a separate vessel eight hundred and forty three (843) pounds of commercial anhydrous sodium ortho silicate, having an Na_2O to SiO_2 ratio of 2:1, are dissolved in three thousand (3000) pounds of water. The temperature of the solution is adjusted to 160° F. The silicate solution is pumped to the crutcher containing the fatty acid mixture. The agitator of the crutcher is rotated at 30 r.p.m. When the ortho silicate solution is introduced into the fatty acid mixture, a double decomposition reaction takes place with the formation of sodium soap of the tallow and coconut oil fatty acids and colloidal silica sol, the silica particles having an $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:4 to 1:2000 or higher.

The consistency of the soap silica mixture can be adjusted by evaporating water or adding water. If the soap mixture is to be dried by chilling on a set of rollers and then passed through a conventional three flight conveyor dryer, the water content is adjusted to the range of 35-40% by weight. The dried ribbon can be milled, plodded and formed into bars using conventional soap making equipment, or milled into powdered soap using a hammer mill or an impact mill.

For spray drying, the viscosity of the soap mixture is adjusted and the mixture can then be injected into the spray tower in accordance with established practice using conventional equipment. The finished soap product can be used for personal cleansing or laundry or other purposes normal to the use of a soap composition as a cleaning agent.

EXAMPLE IV

One thousand and fifty (1050) pounds of sodium silicate solution having an Na_2O to SiO_2 ratio of 1:3.22 (Na_2O content of 8.90% and an SiO_2 content of 28.7%) are diluted with three thousand (3000) pounds of water and heated to 140° F. in a closed vessel. In a separate mixing vessel nine hundred (900) pounds of dodecyltetrapolyoxyethylene acid sulfate is heated to 140° F. The heated sodium silicate solution is pumped to the vessel containing the acid sulfate solution. Agitation is provided by a turbine agitator operating at 60 r.p.m. a pumping rate of silicate solution is maintained at 50 gal./min.

A double decomposition reaction occurs rapidly as the silicate solution is mixed with the acid sulfate, with the formation of a colloidal silica sol, having an Na_2O to SiO_2 ratio of 1:4 to 1:2000 and an average ratio of approximately 1 to 500. After a period of 30 minutes the reaction mass is cooled to about 75° F.

As a result of the reaction, the acid sulfate is converted to an aqueous solution of its sodium salt (dodecyltetrapolyoxyethylene sodium sulfate) containing a colloidal silica sol.

The final pH of the reaction is adjusted to 10.8 by addition of alkyl acid sulfate if the pH is high or sodium silicate if the pH is low.

The cooled reaction product is colloid milled at a rotor-stator gap setting of 0.035 inch and later at 0.004 inch to break up agglomerates of colloidal silica and bring the reaction to completion. Frequently, the milling treatment lowers the pH to 10.5 which is within the desired range.

The reaction product may be used for removal of soil from fabrics or hard surfaces at elevated or ambient temperatures. Ancillary detergent additives may be employed with the reaction products or they can be used alone diluted with water.

EXAMPLE IV

The present example is presented for the purpose of illustrating the effectiveness of the colloidal sol-detergent compositions of the present invention in adsorbing and transporting particulate soils.

The following compositions in Table I were prepared comprising the components designated:

TABLE I

Pounds of.....	A	B	C
Product of Example I (940 lbs. sodium dodecyl benzene sulfonate, 60 lbs. colloidal silica).....	1,000	1,000	1,000
Sodium dodecyl benzene sulfonate.....	50.0	50.0	50.0
Methylene dinaphthylene sodium sulfonate.....	200.0	200.0	200.0
Nonylphenolpolyoxyethylene ethanol.....	20.0	20.0	20.0
Ethylene diamine trisodium acetate ethanol.....	6.5		
Polystyrene sodium sulfonate (2,500,000 molecular weight).....	50.0	50.0	50.0
Hydrotrope (sodium xylene sulfonate).....	2.0	2.0	2.0
Optical brighteners (diamino stilbene).....			

Aquadag, a water dispersible colloidal graphite produced by the Acheson Graphite Company, in the amount

of 0.02 gm. was dispersed in 500 ml. of 0.2% solution of compositions A, B and C referred to in Table I. The same amount of Aquadag was also dispersed in 500 ml. of distilled water.

The dispersions were allowed to remain at ambient temperature for one hour and were then filtered through Whatman No. 5 filter paper. The filtrates were collected and examined for their relative optical densities using a series of Nessler tubes. Ten milliliters of filtrate were employed as a basic standard and then diluted with measured amounts of distilled water to reach the optical densities of all specimens.

Using the 10 ml. of the distilled water Aquadag filtrate diluted to 50 ml. as a standard and assigned an optical density of 1, the filtrates, based on the respective detergent compositions of Table I, yielded the following optical densities, indicating the ability of the compositions to transport the graphite and, correspondingly, soil through a tight matrix such as analytical filter paper and/or fabric.

	Optical density
Distilled water composition	1
A	1.5
B	1.2
C	1.33

Thus, it can be seen that organic detergent used in B, in the absence of the colloidal silica, transports colloidal graphite particles through the pores of filter paper better than water. However, the colloidal silica sol dispersions of this invention in combination with the same organic detergent solution, as illustrated in Examples A and C, materially improve the transport of the colloidal graphite, as compared to the water and the organic detergent solution alone of Example B. The improvement of composition A over C is attributed, in part, to the presence of a minor amount of polystyrene sodium sulfonate, generally used between about 0.1 to 2.0 percent. Such alkali sulfonates have been found to exert a synergistic influence on the surface activity of organic detergents and also a positive influence on the stability of colloidal dispersions.

As demonstrated, the colloidal silica sol-detergent combination of composition C carries colloidal graphite solids through a tight filter matrix approximately ten percent better than the same detergent composition without silica sol. Composition A, also containing the silica sol, exhibits a twenty-five percent improvement over composition B without colloidal silica sol.

The foregoing phenomena has an important bearing upon and indicates the ability of a detergent composition in the removal of soil from a fabric or other matrix and the prevention of redeposition of the soil onto the fabric or matrix from which it was removed.

Soil removal efficiency and soil redeposition test results on fabrics and the influence of the presence of colloidal silica sols in the wash water on soil removal and prevention of soil redeposition are further demonstrated by the data present below.

A series of ten loads of moderately soiled clothes, primarily towels and bed linens washed in a top loading type domestic washing machine which employed a fifteen minute wash cycle and a five minute rinse cycle.

Compositions	Cleaning efficiency (average of 10 loads)
A..... $\frac{3 \times 5}{3 \times 5} \times 100 =$	100 Excellent.
B..... $\frac{3 \times 4}{3 \times 5} \times 100 =$	80 Fair.
C..... $\frac{3 \times 4.5}{3 \times 5} \times 100 =$	90 Good.

Cleaning efficiency is determined by the following relationship:

Condition before washing: Condition after washing:
 1—Slightly soiled 1—Still heavily soiled
 3—Moderately soiled 3—Moderately soiled
 5—Heavily soiled 5—Completely clean

$$\frac{\text{Initial} \times \text{final}}{\text{Initial} \times \text{maxim.}} 100 = \text{percent cleaning efficiency}$$

Soil redeposition was determined by the percent loss of reflectance of clean specimens of Indianhead cotton washed in a Terg-O-Tomer apparatus employing the following operating conditions:

Soil: 0.2 cc. of 10% solution Aquadag
 Detergent: 0.2% solution (1 liter)
 Cycle: 10 minutes
 Temperature: 120° F.

Detergent:	Percent loss reflectance
Composition A -----	25
Composition B -----	30
Composition C -----	26
Water -----	61

These values accord well with the transport values determined with Aquadag colloidal graphite. The influence of the colloidal silica formed as contemplated herein on the prevention of soil redeposition is apparent.

Having described the invention and certain exemplary embodiments, the same is only intended to be limited by the scope of the following claims.

What is claimed is:

1. A method for making a detergent composition which comprises reacting a water soluble alkali silicate with an aqueous solution of an anionic detergent-forming acid in such proportion as to yield in situ a composition not greater than 0.2 N in alkali ion, the said composition comprising as products of said reaction an anionic detergent and a colloidal silica sol alkali-stabilized within a pH range of 7.2 to 11.0.

2. The method of claim 1 wherein said alkali silicate and said acid are separately preheated to a temperature within the range of about 120° to 160° F. prior to reaction.

3. The method of claim 1 which additionally comprises the step of adding to said composition comprising said colloidal silica sol from about 0.1 to about 2.0% by weight polystyrene sodium sulfonate based upon the weight of non-water components of said composition.

4. The method of claim 1 wherein said silica sol is characterized by an alkali oxide to SiO₂ ratio of 1:4 to 1:2000.

5. The method of claim 4 wherein said acid is selected from the group consisting of fatty acids having from 8 to 22 carbon atoms in the carbon chain and alkyl aryl sulfonic acids.

6. The method of claim 5 wherein said alkali silicate is selected from the group consisting of sodium and potassium silicates having an alkali oxide to SiO₂ ratio greater than 1:4.

7. The method of claim 5 wherein said acid is dodecyl benzene sulfonic acid.

8. The method of claim 5 which additionally comprises the step of adding to said composition containing said colloidal silica sol from about 0.1 to about 2.0% by weight polystyrene sodium sulfonate based upon the weight of the non-water components of said composition.

9. The method of claim 6 wherein said acid is dodecyl benzene sulfonic acid.

10. The method of claim 7 which additionally comprises the step of adding to the said composition containing said colloidal silica sol from about 0.1 to about 2.0% by weight polystyrene sodium sulfonate based upon the weight of the non-water components of said composition.

References Cited

UNITED STATES PATENTS

3,223,646	12/1965	McKenna et al.	252—135
3,454,499	7/1969	Meyer et al.	252—109
2,443,512	6/1948	Powers et al.	252—513 X
2,532,497	12/1950	Hoekstra	252—317 X
2,649,388	8/1952	Wills et al.	117—103
2,677,665	5/1954	James	252—131

FOREIGN PATENTS

559,137	2/1944	Great Britain	252—138
943,405	12/1963	Great Britain	252—109
152,460	7/1953	Australia	23—182
470,699	8/1937	Great Britain	252—317
551,616	3/1943	Great Britain	252—138

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