United States Patent Office 3,306,858
Patented Feb. 28, 1967

3,306,858

PROCESS FOR THE PREPARATION OF STORAGE STABLE DETERGENT COMPOSITION

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No Drawing. Filed June 17, 1965, Ser. No. 464,821
3 Claims. (Cl. 252—99)

This application is a continuation-in-part of my copending application, Serial No. 207,804, filed July 5, 1962, now abandoned.

This invention relates to detergent compositions which are particularly useful in dishwashing applications.

For some time efforts have been made in the art to combine organic surface active agents and chlorine releasing agents in a single granular dishwashing product. Both of these materials have certain properties which are desired in dishwashing detergents and the combination of these agents with other conventional detergent constituents results in an eminently superior dishwashing detergent. The organic surface active agents function to emulsify food soils, to inhibit foam caused by food soils, to promote wetting of dinnerware thereby eliminating or minimizing spotting and to improve generally the overall detergency of the composition for soil removal. Agents or chemicals which release oxidizing chlorine contribute to the improvement of the detergent composition by virtue of their oxidizing action on food soils, particularly proteins, to convert them to a more soluble form. The chlorine releasing agents also exert a bleaching action on dinnerware to remove stains such as are caused by coffee and tea and also prevent a build-up of soil films on the dinnerware surfaces thereby curtailing spotting.

While the advantages of combining non-ionic surface active agents and chlorine releasing agents in a single dishwashing product have been long recognized, considerable difficulties have been encountered in so doing. The surfactants normally used in these detergent formulations are organic non-ionic polyether type materials which are readily susceptible to attack by chlorine and particularly the hypochlorite ion. As a consequence of such reactions, the surfactants break down and in a relatively short period lose the aforementioned desirable properties. The chlorine is also dissipated as a result of reaction with the surfactants so that by the time the detergent product is used by the ultimate consumer it frequently is substantially devoid of the desirable properties imparted by both the surfactant and the chlorine releasing agents.

The present invention provides a means for preparing detergent compositions suitable for dishwashing applications in which organic non-ionic surface active agents are compounded with chlorine releasing agents to form a suitable product which may be stored indefinitely without undesired reaction between these normally incompatible components. By the method of the present invention detergent compositions can be prepared which exhibit none of the aforementioned undesirable characteristics although such compositions comprise the constituents set forth hereinbefore.

In general, this process comprises incorporating an organic surface active agent with a solid carrier material and then applying thereto a coating which effectively protects and prevents the surfactant from reaction with chlorine during storage of the composition. After coating or encapsulating the surfactant in suitable manner, it can then be combined with the chlorine releasing agent and other constituents normally used in formulating dishwashing type detergents. The constituents of such detergents generally include an alkaline detergent salt, an alkaline condensed phosphate salt and a chlorine releasing agent. Examples of alkaline detergent salts used in washing detergents are di-, tri- and tetra-sodium orthophosphates, sodium carbonate, sodium bicarbonate, alkali metal silicates such as sodium silicate, alkali metal borates such as sodium borate, alkaline condensed phosphate salts such as tetrasodium pyrophosphate or tetrapotassium pyrophosphate and polyphosphates such as sodium tripolyphosphate. Suitable chlorine releasing agents include chlorinated trisodium phosphate which is a composition consisting of trisodium phosphate and sodium hypochlorite in intimate association in a crystalline form; potassium dichloroisocyanurate, trichloro melamine, Chloramine T, sodium, calcium and lithium hypochlorites, dichlorocyanuric acid, trichlorcyanuric acid, dichlorodimethyl hydantoin and the like.

The surface active agents useful in the detergent compositions of the invention are the normally liquid organic non-ionic surface active agents obtained by condensing alkylene oxides with water-insoluble organic compounds such as organic hydroxy compounds, that is alcohols, phenols, thiols, primary and secondary amines, carboxylic and sulfonic acids and their amides. Surfactants of this type are well known in the art and a variety of these agents are commercially available under various trade names, as for example the Pluronics (condensates of ethylene oxide with a hydrophobic base formed by condensing propylene oxide with propylene glycol), Hyonics (e.g. fatty alkylolamides), Triton X–100 (a condensate of isooctyl phenol with about 8 moles of ethylene oxide). One non-ionic surfactant which has been employed in the specific examples to illustrate the present invention is a polyoxyalkylene polymer obtained from the Tretolite Co. of St. Louis, Missouri under the designation of "Product E–97." This polyoxyalkylene polymer has the formula:

$$HO(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H_2{-}O)_x{-}(CH_2CH_2O)_y{-}(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H_2O)_x{-}(CH_2CH_2O)_y{-}(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H_2O)_x{-}H$$

where x, y and z are integers such that the average molecular weight of the compound ranges from about 3600 to 4400. Its chemical and physical characteristics are:

Cloud point: 33°–34° C.
Refractive index: 1.4555
Hydroxyl value: 28.9 mg. KOH/g. sample
Specific gravity: 1.038–1.041
Average molecular weight: 3600–4400

In the practice of the present invention a suitable organic non-ionic surfactant is mixed with granular particles of a water-soluble solid carrier material with agitation so that the carrier particles absorb the liquid surface active agents. According to a preferred embodiment the liquid organic non-ionic surfactant is absorbed on a water-soluble carrier material selected from the group consisting of tetrasodium pyrophosphate, tetrapotassium pyrophosphate, disodium orthophosphate, trisodium orthophosphate, sodium carbonate, sodium bicarbonate, alkali metal silicates, alkali metal borates, sodium tripolyphosphate and sodium hexametaphosphate. After incorporating a suitable proportion of the non-ionic surfactant with the carrier, the carrier particles are sprayed or otherwise coated with a suitable coating material such as liquid silicates and the like. In a preferred procedure, the carrier particles on which the organic non-ionic surfactant is absorbed are coated by means of an aqueous solution of a compound selected from the group consisting of tetrasodium pyrophosphate, tetrapotassium pyrophosphate, sodium tripolyphosphate and sodium hexametaphosphate. Coating of the non-ionic surfactant-inorganic salt particles is effected in any convenient manner

such as by slowly adding the aqueous coating solution from a dropping funnel to form an encapsulating coating thereon. Preferably, the coating is applied utilizing a fine spray together with thorough agitation of the carrier particles. The combination of fine spray and substantial agitation produce the optimum coating effect.

After application of the coating solution, the granular carrier particles containing the non-ionic surfactant are suitably coated and are then dried by any suitable means such as air drying or by incorporating with the wet coated particles additional quantities of a dry inorganic salt constituent to absorb the excess coating solution. Other drying agents such as sodium carbonate and the like can also be employed. The coated or encapsulated non-ionic surfactant-salt particles can then be admixed in suitable proportions with the remainder of the detergent constituents including the chlorine releasing agents to form a final detergent product which remains stable until use. The chlorine releasing agents are not incorporated into the detergent formulation until after the non-ionic surfactant has been protected by encapsulation.

EXAMPLE I

9.7 parts of the above indicated liquid non-ionic surfactant and 53.3 parts of anhydrous granular sodium tripolyphosphate were placed in a kitchen type food blender and thoroughly mixed. After mixing for several minutes, 35 parts of a 60% aqueous solution of tetrapotassium pyrophosphate were slowly added from a dropping funnel to the particles in the mixer while they were being agitated during a period of about 10 minutes. During this tetrapotassium pyrophosphate addition, the temperature of the mixture rose from 75 to 103° F. indicating hydration of the tripolyphosphate. Any agglomerates formed were broken up and the product dried by means of air.

The above encapsulated product or "pre-mix" was then admixed with other conventional constituents including a chlorine releasing agent to form a dishwashing detergent having the composition:

Formulation I

	Parts
Pre-mix	10.3
Anhydrous sodium metasilicate	24.0
Sodium tripolyphosphate	14.3
Potassium dichloroisocyanurate	1.0
Sodium carbonate	50.4

EXAMPLE II

Following the above procedure, 11.3 parts of the non-ionic surface active agent was mixed with 63.7 parts sodium tripolyphosphate and 25 parts of a 60% aqueous solution of tetrapotassium pyrophosphate was added as the coating material.

The encapsulated "pre-mix" was blended with other constituents to form a dishwashing detergent having the composition:

Formulation II

	Parts
Pre-mix	8.9
Anhydrous sodium metasilicate	24.0
Sodium tripolyphosphate	15.1
Potassium dichloroiocyanurate	1.0
Sodium carbonate	51.0

EXAMPLE III

11.3 parts of the non-ionic surface active agent were mixed with 63.7 parts sodium tripolyphosphate in a 16 quart twin shell mixer. After absorption of the liquid surfactant on the tripolyphosphate particles, 25 parts of a 60% aqueous solution of tetrapotassium pyrophosphate was sprayed on the mixture in order to apply a coating to the particles. During this addition the temperature of the mixture rose from about 80 to 92° F. The agglomerates which formed were broken up and the product air dried.

The above encapsulated product or pre-mix was admixed with other constituents to form a dishwashing detergent having the composition:

Formulation III

	Parts
Pre-mix	8.9
Anhydrous sodium metasilicate	24.0
Sodium tripolyphosphate	15.1
Potassium	1.0
Sodium carbonate	51.0

EXAMPLE IV

9.3 parts of the non-ionic surface active agent and 86.5 parts of sodium tripolyphosphate were thoroughly mixed in a ribbon mixer. After thorough mixing, 4.2 parts of a 60% aqueous solution of tetrapotassium pyrophosphate was sprayed on the particles under pressure during a period of about 10 minutes. During this addition, the temperature of the mixture rose from about 75 to 108° F. Drying of the mixture was accomplished by adding solid tetrapotassium pyrophosphate to absorb the excess moisture.

The above encapsulated product or pre-mix was admixed with other constituents to form a dishwashing detergent having the composition:

Formulation IV

	Parts
Pre-mix	10.8
Anhydrous soduim metasilicate	37.4
Potassium dichloroisocyanurate	1.0
Hydrated sodium tripolyphosphate	7.6
Sodium tripolyphosphate	12.9
Sodium carbonate	30.3

The detergent formulations in the above Examples I through IV are prepared in accordance with the invention. Other detergent compositions were prepared as follows:

EXAMPLE V

Following the same procedure as in Example I, 11.9 parts of the non-ionic surfactant and 67.6 parts of sodium tripolyphosphate were mixed and then 21.5 parts of water added in lieu of the 60% aqueous tetrapotassium pyrophosphate of Example I. Accordingly no coating or encapsulation of the non-ionic was effected.

The above pre-mix was combined with other constituents to form a composition:

Formulation V

	Parts
Pre-mix	8.4
Anhydrous sodium metasilicate	24.0
Sodium tripolyphosphate	15.4
Potassium dichloroisocyanurate	1.0
Sodium carbonate	51.2

EXAMPLE VI

14.9 parts of the non-ionic surfactant were mixed with 85.1 parts sodium tripolyphosphate. No encapsulation of the surfactant was accomplished. This pre-mix was combined with other constituents to form the composition:

Formulation VI

Pre-mix	6.7
Anhydrous sodium metasilicate	24.0
Sodium tripolyphosphate	16.3
Potassium dichloroisocyanurate	1.0
Sodium carbonate	52.0

EXAMPLE VII

A pre-mix was made according to the following formula:

9.7 parts of a liquid non-ionic surfactant (Product E–97 above)

53.3 parts of carrier material (carrier materials listed below)

35.0 parts of 60% solution of tetrapotassium pyrophosphate

The above pre-mix was made out of the following inorganic substances substituted as the carrier material: tetrasodium pyrophosphate, disodium orthophosphate, trisodium orthophosphate, sodium carbonate, sodium metasilicate, sodium tripolyphosphate and sodium hexametaphosphate.

The above pre-mixes are incorporated into a formulation which contains the following ingredients:

	Parts
Pre-mix	10.3
Anhydrous sodium metasilicate	24.0
Sodium tripolyphosphate	14.3
Potassium dichloroisocyanurate	1.0
Sodium carbonate	50.4

EXAMPLE VIII

A pre-mix was made as follows:

	Percent
Sodium tripolyphosphate	58.6
Liquid non-ionic surfactant (Product E–97 above)	10.3
Sodium metasilicate	31.1

The above pre-mix was incorporated into a formula as follows:

	Percent
Pre-mix	10.0
Light ash	45.0
Sodium metasilicate anhydrous	21.4
Dense ash (sodium carbonate)	8.0
Sodium tripolyphosphate	14.3
Potassium dichloroisocyanurate	1.3

It has been pointed out hereinbefore that in detergents prepared in accordance with prior art procedures the non-ionic surface active agents are attacked by chlorine during storage with consequent loss in desirable properties of the detergent including its defoaming properties. Since this characteristic can be appropriately evaluated through practical use in automatic dishwashing machine, this medium was employed to compare the defoaming stability of detergents prepared in accordance with this invention and detergents not so prepared.

A Hobart AM commercial dishwashing machine was employed for the defoaming test. Samples of the detergent compositions were stored in a container at 98° F. and weighed samples withdrawn for the test at various intervals. The detergents were employed in the defoaming test in a concentration of 0.4 percent in the presence of 0.1 percent raw egg soil. The test itself consists of recording the water pressure by a differential manometer connected to a pitot tube that is inserted into the wash arm of the dishwashing machine. A higher water pressure indicates greater defoaming action by the detergent. Utilizing this test procedure, the defoaming performance of various detergent formulations are shown below in Table 1.

and VI, which were prepared in accordance with prior art procedures.

From observing Table 1 it is seen that there is a large difference between stability of Formulations I and II made with the encapsulated pre-mix as described in the present application as compared to the Formulation V which is an example in which there is no encapsulation. In this case, after 77 days the 2 formulations containing the encapsulated pre-mix still showed considerable amounts of stable chlorine and defoaming ability, whereas the formulae containing no encapsulated pre-mix have dropped to 14 millimeters. The same is true for Formulations III and IV as compared to Formulation VI. Formulations III and IV also contain an encapsulated pre-mix, whereas Formulation VI contains a pre-mix made without encapsulation.

The outstanding chloric stability of the detergents prepared in accordance with the invention is also shown by comparison with detergents prepared by prior art processes. Detergents were stored at room temperature for varying periods and when the detergent was dissolved in water the chlorine available was determined by titration. For this comparison detergent Formulations VII and VIII were prepared in which the non-ionic surfactant was mixed with the sodium carbonate after which the other constitutents of the composition were mechanically mixed therewith. The non-ionic surfactants were not encapsulated or protected according to the present invention.

Formulation VII

	Parts
Sodium carbonate	52.0
Non-ionic	2.20
Anhydrous sodium metasilicate	24.0
Sodium tripolyphosphate	20.0
Potassium dichloroisocyanurate	1.8

Formulation VIII

	Parts
Sodium carbonate	22.72
Non-ionic	2.08
Anhydrous sodium metasilicate	43.16
Potassium dichloroisocyanurate	1.71
Hydrated sodium tripolyphosphate	7.61
Sodium tripolyphosphate	22.72

A comparison of the chlorine stability of the above formulations with detergent Formulations II and VI of the present invention are shown below in Table 2.

TABLE 2.—CHLORINE STABILITY

[Storage conditions—room temperature]

Storage Time, days	Percent Available Chlorine		Storage Time, days	Percent Available Chlorine	
	Formulation II	Formulation VII		Formulation VI	Formulation VIII
0	0.55	0.92	0	0.58	0.92
170	0.48	0.44	125	0.55	
			130		0.35

TABLE 1

Storage Time, days	Detergent Formulation, I, mm.	Detergent Formulation, II, mm.	Detergent Formulation, V, mm.	Storage Time, days	Detergent Formulation, III, mm.	Detergent Formulation, VI, mm.	Storage Time, days	Detergent Formulation, IV, mm.
0	49	35	30	0	57	56	0	58
21	39	39	31	28	61	36	35	52
49	50	49	27	56	47	35	50	51
63	50	39	13	84	50	28	80	51
77	51	42	14	97	51	16	115	49
				107	49	18		

It may be readily seen from the above test data that the process of the present invention results in detergent products having remarkably superior defoaming properties. Thus, after extended periods of storage, the defoaming properties of detergent Formulations I, II, III and IV, which were prepared in accordance with the present invention, were far superior to detergent Formulations V

As seen, the available chlorine in the detergent of the present invention remained substantially constant after storage whereas the prior art detergents, as a result of storage, suffered a loss in available chlorine.

Those modifications and equivalents which fall within the spirit of the invention and the scope of the appended claims are to be considered part of the invention.

I claim:

1. A process for preparing a storage-stable detergent composition which process comprises absorbing a liquid organic non-ionic surface active agent on a solid carrier material selected from the group consisting of tetrasodium pyrophosphate, tetrapotassium pyrophosphate, disodium orthophosphate, trisodium orthophosphate, sodium carbonate, sodium bicarbonate, alkali metal silicates, alkali metal borates, sodium tripolyphosphate and sodium hexametaphosphate, and then with agitation contacting said carrier material on which the said organic surface active gent is absorbed with an aqueous solution of a compound selected from the group consisting of tetrasodium pyrophosphate, tetra-potassium pyrophosphate, sodium tripolyphosphate and sodium hexametaphosphate to form thereon an encapsulating coating, drying said encapsulated material and thereafter mixing said encapsulated material with a chlorine releasing agent.

2 A process according to claim 1 wherein said chlorine releasing agent is selected from the group consisting of chlorinated trisodium phosphate, chlorinated cyanurates and chlorinated amines.

3. A process for preparing a storage-stable detergent composition which comprises absorbing a liquid organic non-ionic surface active agent on solid particles of sodium tripolyphosphate and then with agitation contacting the particles on which the surface active agent is absorbed with an aqueous solution of tetrapotassium pyrophosphate to form thereon an encapsulated coating, drying said encapsulated material and thereafter mixing said encapsulated material with a chlorine releasing agent.

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