

UNITED STATES PATENT OFFICE

2,577,773

TERNARY DETERGENT COMPOSITIONS

Joseph M. Lambert, Easton, Pa., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application March 26, 1947,
Serial No. 737,437

3 Claims. (Cl. 252-152)

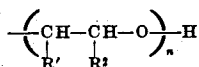
1

This invention relates to an improved germicidal detergent composition comprising a mixture of one of the usual organic anionic active detergents, an organic cationic active germicide and a nonionic organic surface active agent.

A number of organic cation active materials which are surface active and possess germicidal properties have found quite extensive use as germicides in cleaning operations such as in the food industry, laundering and the like. However, it has been necessary to employ these cation active germicides as a separate rinse or wash, since efforts to combine them with the usual organic anion active detergents in a single wash have heretofore been unsuccessful. When the organic anion active detergent is combined with a cation active germicide in a single wash, the mixture not only is objectionable because of its appearance (inhomogeneity, cloudiness, separation into layers or formation of precipitates), but in addition the detergent power of the mixture is generally noticeably lower than that of the anion active detergent and the germicidal power of the cation active germicidal compound is adversely affected, such mixtures in practically all cases showing noticeably less germicidal activity and at times none at all.

I have now found that the addition of a small amount of an organic nonionic surface active agent to a mixture of a surface active germicidal cation active material and an organic anionic detergent makes the cation active and anion active compounds compatible, so that not only is the formation of cloudiness or precipitation prevented but in addition the germicidal activity of the mixture is substantially equal to that of the cation active agent alone and the detergency of the mixture is in no way adversely affected and frequently is improved.

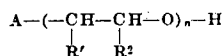
The nonionic surface active agents which I have found to be effective for incorporation in mixtures of organic anionic detergents and cation active germicides are viscous liquid to wax-like water-soluble surface active materials containing a polyether group of the type



in which R' and R² are hydrogen or alkyl. The nonionic surface active agents employed are obtained by replacing with a polyglycol ether group an active hydrogen atom of a monomeric organic compound containing at least 6 carbon atoms and an active hydrogen, such as carboxylic acids, amides, amines and organic hydroxy compounds (phenols and alcohols). These water-

2

soluble nonionic surface active agents may be represented by the following general formula:



wherein A represents a residue of a compound selected from the group consisting of a monomeric organic compound containing an active hydrogen atom (i. e. alcohols and phenols, amides, primary and secondary amines and carboxylic acids) and R' and R² represent hydrogen or alkyl, and n is an integer greater than three (i. e. the number of alkyleneoxy groups in the polyglycol ether radical is sufficient to impart water-solubility to the product; the exact number of such groups will therefore vary with the particular compound employed but as a general rule at least 1 alkyleneoxy group should be present in the polyglycol ether group for each 2 carbon atoms in the parent compound). Such nonionic surface active agents are well known in the art, having been described, for instance, in U. S. Patent No. 1,970,578 to Schoeller et al. and No. 2,213,477 to Steindorff et al. and may be exemplified by the polyalkylene oxide derivatives (i. e. polyethylene oxide, polypropylene oxide, polybutylene oxide) of water-insoluble higher fatty acids, such as lauric, oleic, palmitic and stearic acid and the like of mixtures thereof, such as the mixtures of fatty acids obtained from animal and vegetable fats and oils or by oxidation of petroleum fractions such as paraffin wax. They may also be exemplified by the polyalkylene oxide derivatives of such water-soluble organic hydroxy compounds as higher aliphatic alcohols (i. e. the alcohols corresponding to the fatty acids specified above or mixtures thereof), oil or phenols, particularly alkyl phenols containing at least six alkyl carbon atoms such as isooctyl, di-tertiary butyl, triisopropyl, nonyl, dodecyl, phenols or naphthols, or of higher alkyl alcohols, such as benzyl alcohol, cinnamyl alcohol and the like and by the polyalkylene oxide derivatives of water-soluble partial vegetable fatty acid esters of anhydro-sorbitol, such as sorbitan monolaurate, sorbitan monostearate and sorbitan monooleate. They may also be exemplified by the polyalkylene oxide derivatives of such amines as stearyl, lauryl, dicyclohexyl, dibutyl amine and the like.

The organic cationic active germicidal materials which form one element of the composition of this invention are those cationic agents which are known to possess germicidal properties and include, by way of illustration, germicidal quaternary ammonium compounds, pyridinium

compounds and the like. Specific compounds of this type are 8-hydroxy-quinolinium sulfate, cetyl pyridinium chloride, octyl-phenoxy ethoxy ethyl (be yl) dimethyl ammonium chloride, alkyl (8 to 18 carbon) dimethyl-3,4-dichlor-benzyl ammonium chloride, alkyl dimethyl benzyl ammonium chloride and the like.

The organic anionic detergents which form another element of the composition of this invention include the usual alkali metal (sodium and potassium) soaps of higher fatty acids of vegetable or animal origin such as hydrogenated cottonseed oil, stearic, lauric, palmitic and similar acids or mixtures thereof of animal or vegetable origin and also the alkali metal soaps of alkyl sulfates and sulfonates, alkylaryl sulfonates and the like, such as sodium cetyl sulfate, hexadecanesulfonic acid sodium salt and diisobutyl-naphthalene-1-sulfonic acid sodium salt.

The relative amounts of organic anionic detergent and cationic surface active germicide which may be employed in the compositions of this invention may be varied through a relatively wide range and as a practical matter, the relative proportions of these two ingredients will depend to a large extent on the specific compounds employed and the specific use for which the composition is intended. Thus, the amount of cationic surface active germicide employed will be such that when the germicidal detergent composition of this invention is added to water for use, the concentration of germicide in the water will be sufficient to give the desired degree of germicidal activity. At the same time the amount of anionic organic detergent employed should be such that when the compound is added to water the detergency of the composition will be satisfactory. When employing the usual alkali metal (sodium and potassium) soaps of higher fatty acids as the organic anionic detergent, the amount of such organic detergent present in the composition of the present invention will generally be in excess of the amount of quaternary-type cationic surface active germicide. However, when employing certain of the newer synthetic organic anionic detergents such as certain alkylaryl sulfonates, satisfactory detergency can frequently be obtained when the cationic surface active germicide is present in excess. Since the relative proportions of the ingredients will vary with the particular agents employed, exact numerical limits cannot be specified except by way of example. However, those skilled in the art can readily determine the optimum proportions for any specific combination of components or specific application by simple preliminary experiments, and as a practical matter the relative proportions of organic anionic detergent and cationic surface active germicide are generally within the range of 1:4 to 12:1.

Likewise, the amount of nonionic surface active agent which is incorporated in the composition of this invention may be varied through a relatively wide range. The relative compatibility of the organic anionic detergents and cationic germicides is evidenced by the turbidity of dilute aqueous solutions thereof such as would be used in cleaning operations. The turbidity of such solutions is particularly pronounced if there exists a 1:1 stoichiometric ratio between the amounts of anionic and cationic agents in the solution. However, the incorporation of approximately 10% of nonionic surface active agent based on the combined weight of the anionic and cationic agents resulted in the formation of

dilute solutions which have very little turbidity and appear almost water-clear. Thus, the mixture of 60 parts by weight of diisobutyl naphthalene-1-sulfonic acid-sodium salt and 40 parts of cetyl pyridinium chloride (total ionic concentration about 0.5 gram per liter) had a turbidity of 64.5 as determined by a Klett colorimeter which reads in $500 \times$ density units, while a solution of the same mixture to which had been added 12% (based on weight of ionic agents) of a water-soluble polyethylene oxide derivative of dibutyl phenol had a turbidity determined in the same manner of 3.5 and a solution of 45 parts by weight of diisobutyl naphthalene-1-sulfonic acid-sodium salt and 55 parts by weight of cetyl pyridinium chloride had a turbidity of 360, while a similar solution to which had been added 12% (based on weight of ionic agents) of a water-soluble polyethylene oxide derivative of diisobutyl phenol had a turbidity of 5.5. While lesser amounts of nonionic surface active agents are effective for improving the compatibility of anionic organic detergents and cationic germicides in dilute aqueous solutions of the type employed in cleaning operations, it has been found that compositions containing such minor amounts of nonionic surface agents are not satisfactory in other respects and as illustrated by the examples below, a substantial amount (about 10%) of the nonionic surface active agent, based on the amount of anionic and cationic agents in the composition should be employed if entirely satisfactory results are to be obtained. Thus, a concentrated solution of these materials such as might be prepared for sale and which contains an amount of nonionic surface active agent of the order of 1% is generally objectionable due to inhomogeneity, cloudiness, separation into layers or the formation of precipitation. However, the appearance of such concentrated solutions can be improved by incorporating a substantial amount of nonionic material therein. Thus, a solution of 20 parts by weight of a potassium fatty acid soap and 2 parts of 8-hydroxy quinolinium sulfate in 78 parts of water was inhomogeneous and separated into a top turbid layer and a clear bottom layer. However, a mixture of 18 parts of potassium soap, 2 parts of 8-hydroxy quinolinium sulfate and 5 parts of water-soluble polyethylene oxide derivative of dibutyl phenol in 75 parts of water was homogeneous and clear. Thus, in general, the ratio of nonionic agent to the combined weight of the ionic agents is within the range of 1:9 to 1:1 and preferably within the range of 1:9 to 2:3.

It has also been found that substantial amounts (about 10%) of such nonionic agents are necessary if the germicidal activity of the composition is to be satisfactory. Table I below illustrates the effect of adding various amounts of the water-soluble polyethylene oxide derivative of di-isobutyl phenol to detergent compositions comprising various mixtures of sodium-N-oleoyl methyl taurate or a conventional sodium soap (Lux flakes), as the anionic organic detergent, with octyl-phenoxy ethoxy ethyl (benzyl) dimethyl ammonium chloride as the cationic germicide. These tests were agar cup-plate tests with *Staphylococcus aureus*, similar to that described at page 957 of the 8th edition of Text Book of Bacteriology by Zinsser and Bayne-Jones using 25 cc. of melted agar per petri dish and cut cups 1.7 cm. in diameter. Thus, a reading of 1.7 cm. means no halos or zero germicidal activity. The parts are by weight.

Table I

Test No.	Composition of Detergent Parts Based on Active Material			Results of Germicide Test, Diameter of Halo in cm.	Amount of Cationic Germicide in Solution (g./liter active material)
	Anionic Organic Detergent	Cationic Germicide	Nonionic Agent		
1.....	5.0	5.0	none	1.7	1.0
2.....	5.0	5.0	10	2.1	0.5
3.....	3.0	7.0	none	2.2	1.0
4.....	3.0	7.0	1.0	2.5	1.0
5.....	3.0	7.0	2.5	2.5	1.0
6.....	6.0	4.0	none	2.2	1.0
7.....	6.0	4.0	1.0	2.3	1.0
8.....	6.0	4.0	2.5	2.4	1.0
9.....	none	10	none	2.4	1.0

The effect of addition of nonionic surface active agents on washing efficiencies of various mixtures of organic anionic detergents and cationic germicides is illustrated in Table I. below. The parts are by weight.

Table II

Test	Composition of Detergent, Parts of Active Ingredients			Wool	Cotton
	Anionic	Cationic	Nonionic	Relative Detergency	
	Na Soap	Octyl-phenoxy ethoxy ethyl (benzyl) dimethyl ammonium chloride			
A.....	6	4	none	63	56
B.....	6	4	1.0	76	108
C.....	6	4	2.5	100	189
	K Soap	8-hydroxy-quinolinium sulfate			
D.....	9	1	none	27	76
E.....	9	1	1.0	81	87
F.....	9	1	2.5	130	108

In Tests A, B and C the anionic detergent employed was a commercial sodium fatty acid toilet soap (Lux flakes) and the cationic germicide employed was octyl-phenoxy ethoxy ethyl (benzyl) dimethyl ammonium chloride. In Tests D, E and F the anionic detergent was a commercial potassium fatty acid soap, the quaternary-type cationic germicide was 8-hydroxy quinolinium sulfate, and in all tests in which a nonionic agent was employed the particular agent used was a water-soluble polyethylene oxide derivative of diisobutyl phenol. The solutions for these tests were prepared in 50 P. P. M. hard water so that the concentration of germicide in Tests A, B and C was 1 gram per liter and in Tests D, E and F 0.2 gram per liter. The tests were made by washing soiled swatches of cloth in a Launder-Ometer for 30 minutes in pint jars with 100 ml. of detergent solution and 10 stainless steel balls ¼" in diameter. The tests on wool were made at 120° F. and the tests on cotton at 160° F. The swatches had been soiled with a mixture of mineral oil, graphite and cottonseed oil suspended in carbon tetrachloride. The reflectance of the swatches before and after washing was determined with a Photo-Volt Reflectometer. The results given in Table II indicate the washing efficiency in terms of relative detergency (RD) calculated from the reflectance data as follows:

$$RD = \frac{(R_f - R_i) \times 100}{R_i}$$

where R_f =reflectance of swatch after washing and R_i =original reflectance of swatch before

washing. Similar tests carried out with cotton washed with 1.5 grams per liter of the sodium soap employed gave a relative detergency value of 160, while similar tests conducted with wool washed with 3 grams per liter of sodium-N-oleoyl methyl taurate gel gave a relative detergency value of 100.

While the compositions described above represent preferred embodiments of the present invention, it will be understood that variations may be made therein as previously indicated. Thus, while the novel germicidal detergent compositions of this invention contain three essential components (an anionic organic detergent, a cationic germicide and a nonionic water-soluble surface active agent containing a polyglycol ether group) they may also contain varying amounts of other compounds customarily incorporated in detergent compositions such as inorganic alkali metal salts such as sodium or potassium phosphates, carbonates, borates and silicates and mutual solvents for water and the surface active agents such as isopropyl alcohol.

I claim:

25 1. A germicidal detergent composition comprising a mixture of an alkali metal fatty acid soap and a germicidal quaternary ammonium compound in relative proportions of from 1:4 to 12:1, said mixture containing a water-soluble nonionic surface active agent having a polyglycol ether group, the ratio of said nonionic agent to the combined weight of said soap and said quaternary ammonium compound being within the range of 1:9 to 1:1.

30 2. A germicidal detergent composition comprising a mixture of an alkyl aryl sulfonate detergent and a germicidal quaternary ammonium compound in relative proportions of from 1:4 to 12:1, said mixture containing a water-soluble nonionic surface active agent having a polyglycol ether group, the ratio of said nonionic agent to the combined weight of said alkyl aryl sulfonate and said quaternary ammonium compound being within the range of 1:9 to 1:1.

35 3. A germicidal detergent composition comprising a mixture of an organic anionic detergent and a germicidal quaternary ammonium compound in relative proportions of from 1:4 to 12:1, said mixture containing a water-soluble nonionic surface active agent having a polyglycol ether group, the ratio of said nonionic agent to the combined weight of said anionic detergent and said quaternary ammonium compound being within the range of 1:9 to 1:1.

JOSEPH M. LAMBERT.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,060,850	Calcott	Nov. 17, 1936
2,089,212	Kritchevsky	Aug. 10, 1937
2,165,356	Dunbar	July 11, 1939
2,184,951	Stotter	Dec. 26, 1939
2,263,948	Halvorsen	Nov. 25, 1941
2,284,086	Ericks	May 26, 1942
2,302,697	Katzman	Nov. 24, 1942

OTHER REFERENCES

Goldsmith, reprint from Chemical Industries entitled "Non-Ionic Surface Active Agents."

Young and Coons, "Surface Active Agents" (1945), pp. 110, 111.