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3,525,696

LOW-FOAMING GERMICIDAL SURFACTANT- IODINE COMPOSITIONS FOR CLEANED-IN- PLACE EQUIPMENT

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No Drawing. Filed Apr. 25, 1966, Ser. No. 544,852
Int. Cl. C11d 3/48, 9/50

U.S. Cl. 252-106

13 Claims

ABSTRACT OF THE DISCLOSURE

A low-foaming surfactant-iodine composition for use in cleaned-in-place equipment, said composition consisting essentially of one part by weight of available iodine, 1 to 4 parts of an anionic surfactant containing a sulfonate grouping and selected from the class consisting of aralkyl sulfonates and N-substituted alkanoyl taurates, .25 to 2 parts of an amphoteric surfactant containing a carboxylate joined through 1 to 4 methylene groups, including methylene groups interrupted by an ether group, to the nitrogen of a moiety selected from the class consisting of fatty alkyl substituted amine and 2-fatty alkyl substituted imidazolium moieties, 12 to 50 parts of an acid selected from the group consisting of phosphoric acid, hydroxyacetic acid, and mixtures thereof, and aqueous-alcoholic diluent in an amount to provide in said composition an available iodine concentration of about 0.5 to 2.5%.

In the cleaning and sanitizing of dairy pipelines and other cleaned-in-place (C-I-P) equipment with surfactant-iodine compositions the vigorous agitation and/or air injection encountered in circulating cleaning and sanitizing solutions amplifies the foaming tendencies of such solutions to the extent that general purpose surfactant-iodine compositions are inoperative in such equipment. Various efforts have therefore been made to provide special low-foaming compositions for such uses, but the results heretofore leave much to be desired.

It is known, for example, that in compositions in which iodine is complexed with water soluble alkyl phenol-ethylene oxide condensate, the foaming in ordinary use situations can be reduced by adding a small amount of water insoluble alkyl phenol-ethylene oxide condensate, but the least foaming of such compositions still foam inoperatively in dairy pipelines and other C-I-P equipment.

Two U.S. patents, Nos. 3,039,916 and 3,150,096, both assigned to applicants' assignee are of special interest in that they recognize the special foam problem in C-I-P equipment and disclose a "dynamic" foam test method which is particularly effective in evaluating extremely low foaming (or essentially non-foaming) products intended for use in C-I-P equipment. The procedure for this "dynamic" foam test method is as follows:

150 ml. of the solution to be tested (a use dilution of a composition containing 6 to 25 p.p.m. of available iodine) is placed in a 500 ml. calibrated gas washing bottle with fritted cylinder. Using an air flow meter, the air flow is adjusted to 2 liters per minute and the foam height is read after equilibrium has been established at a temperature of 25° C.

When tested by this method, a composition, to be suitable for use in C-I-P equipment, must have a foam rating of less than 125 ml., and preferably below about 75 ml.

In U.S. Pat. No. 3,039,916 it is disclosed that in germicidal compositions wherein iodine is complexed with certain alkanoyl taurate compounds the foaming of use dilutions of such compositions can be reduced by including a small amount of a nonylphenol ethylene oxide con-

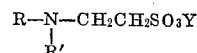
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densate containing about 1.5 mols of ethylene oxide per mol of nonylphenol (which is water-insoluble). With such compositions, however, both the iodine and the water insoluble alkyl phenol ethylene oxide condensate concentrate in the foam, resulting in the formation of a highly insoluble brown tar. This tar coats equipment being cleaned preventing proper rinsing, and is frequently more difficult to remove than the original soil.

U.S. Pat. No. 3,150,096 provides a low-foaming iodine composition intended for use in C-I-P equipment in which an anionic surfactant, sodium xylene sulfonate, is combined with a polymeric material, sodium polymethacrylate, in an acid system. While this composition is a very low-foam composition, it has been found to be unsatisfactory as a cleaning composition when used in the field due to its poor detergent action. Furthermore, the iodine complexing is very poor, with the result that iodine odor of use dilutions makes such compositions impractical for use even as sanitizing rinses.

It is now discovered, in accordance with the present invention that extremely low foaming, or essentially non-foaming, surfactant-iodine compositions can be prepared, which rinse clean without forming any brown tarry deposits, and which have good cleaning and detergent properties, by employing as surfactant component a mixture of certain anionic and amphoteric surfactants in the general proportions of about 1 to 4 parts by weight of anionic surfactant to each part by weight of amphoteric surfactant, with the 4:1 ratio being preferred in instances where both cleaning and sanitizing are desired; and further including in a composition an acidifying agent which will provide a pH below 3.5 in intended use dilutions of the compositions, i.e. dilutions containing 6 to 25 p.p.m. available iodine.

Anionic surfactants suitable for use in the new compositions are those characterized as containing a sulfonate group, with a preferred type being alkanoyl taurates of the formula:



where R is the radical $\text{C}_x\text{H}_{2x+1}\text{CO}$, x being an integer from 5 to 17, R' is selected from the group consisting of hydrogen, lower (C_1 to C_4) alkyl and cyclohexyl radicals, and Y is selected from the group consisting of hydrogen and salt forming cations such as sodium, potassium and ammonium. Typical examples of such compounds, commercially available under the trademark Igepon include:

Igepon CN-42—Sodium N-cyclohexyl-N-palmitoyl-taurate

Igepon T-33—Sodium N-methyl-N-oleoyl-taurate

Igepon TC-42—Sodium N-coconut acid-N-methyl-taurate

Other suitable anionic surfactants include alkali metal alkyl aryl sulfonates such as C_8 - C_{16} alkyl benzene and C_6 - C_{12} alkyl naphthalene sulfonates, of which sodium dodecylbenzene sulfonate (available as Nacconol N.R.S.F.) is representative, and sodium dodecyl diphenyl ether disulfonate (available as Benax 2A1).

Amphoteric surfactants suitable for use in the new compositions are those characterized as containing a carboxylate moiety joined through 1 to 4 methylene groups (including methylene groups interrupted by an ether group) to a substituted amine moiety with a substituent of said amine moiety including a fatty alkyl group. Typical examples of such amphoteric surfactants include N-fatty alkyl B-imino and B-amino propionic acids and their salts of the general formula:

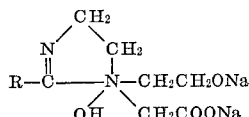


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wherein R is fatty alkyl, R' is the group $-\text{CH}_2\text{CH}_2\text{COOX}$ where X is H or a salt forming cation such as sodium, potassium, or ammonium, and R² is selected from the group consisting of hydrogen, fatty alkyl (not necessarily the same as R) and R'. Typical examples of such compounds, commercially available under the trademark Deriphat include:

Deriphat 151—Sodium N-coco B-aminopropionate
Deriphat 154—Disodium N-tallow-B-iminodipropionate
Deriphat 160—Disodium N-lauryl-B-iminodipropionate
Deriphat 170C—N-lauryl-N-myristyl-B-aminopropionic acid

Other suitable amphoteric surfactants are substituted imidazolium compounds of the formula



in which R is a fatty alkyl group containing 9 to 17 carbon atoms.

Compounds of this type, which are disclosed in U.S. Pat. 2,528,378 are commercially available under the trademark Miranol, typical examples being:

Miranol-CM—where R is $\text{C}_{11}\text{H}_{23}$ derived from coconut acid

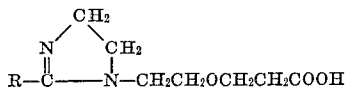
Miranol-HM—where R is $\text{C}_{11}\text{H}_{23}$ derived from lauric acid

Miranol-OM—where R is $\text{C}_{17}\text{H}_{35}$ derived from oleic acid

Miranol-SM—where R is C_9H_{19} derived from capric acid

Miranol-DM—where R is $\text{C}_{17}\text{H}_{35}$ derived from stearic acid

Also suitable are the closely related imidazolium compounds of the formula:



where R is C_9 to C_{17} fatty alkyl, and alkali metal salts thereof.

In preparing the new compositions elemental iodine can be dissolved in a mixture of the surfactants with heating and agitation, but the iodine is more easily introduced as an aqueous HI-iodine solution (iodine dissolved in concentrated—45% or higher—hydriodic acid) suitably containing about 57% available iodine. The concentration of available iodine in the composition can be varied considerably depending on the amount of dilution desired for preparation of use dilutions. For the practical dilution rate of one ounce per 5 gallons of water (1 part composition to 640 parts by volume of water) an available iodine concentration in the range of .5 to 2.5% is generally preferred. Since compositions of somewhat higher or lower available iodine content can be employed equally well, by merely modifying the dilution rate, the relative amounts of surfactants and acid present are best considered with reference to the amount of available iodine.

The amount of acid in the new compositions, which can suitably be phosphoric acid, hydroxyacetic acid, or mixture thereof, can vary substantially with variations in available iodine concentration and intended use dilution. It is known that these acids protect the iodine in the presence of hard water components and organic soil, but in the new compositions the acid, in an amount to provide a pH below 3.5 at use dilution, has a critical effect on the foaming characteristics. Between pH 3.5 and pH 4.0 the anionic-amphoteric surfactant mixture at use dilution shows a marked increase in foaming tendencies which would render the compositions unsuitable for C-I-P cleaning and sanitizing purposes. As a point of reference a composition containing 1.88% available iodine by weight, and intended for use dilutions of about 25 p.p.m. avail-

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able iodine, should contain about 30 to 40% of acid (on a 100% active basis). This amount of acid will provide a pH below 3.5 in most varying water conditions from distilled water to F.D.A. hard water (Federal Register Sept. 19, 1956).

When the compositions are acidified with phosphoric acid it is desirable to employ conventional phase stabilizing components, i.e. to prevent any precipitation on standing, such as a lower alcohol or glycol. As much as about 20% of isopropyl alcohol or 10% by weight of propylene glycol can be employed, although as part or all of the phosphoric acid is replaced by hydroxyacetic acid, the alcohol or glycol can be substantially reduced, since compositions acidified with hydroxyacetic acid are more phase stable. This coupled with the lower corrosiveness of hydroxyacetic acid tends to offset the substantially higher cost of hydroxyacetic acid as the acidifying agent.

Having reference, thus, to compositions containing .5 to 2.5% available iodine, and intended to be diluted with water to use dilutions of about 6 to 25 p.p.m. available iodine the proportions of active components on a 100% active basis should be:

	Parts by wt.	Parts by wt. preferred
Component:		
Available iodine.....	1	1
Anionic surfactant.....	1-4	2-2.5
Amphoteric surfactant.....	25-2	.5-1
Acid.....	12-50	15-30

It is significant to note that the proportion of total surfactant to iodine ranges from 1.25:1 to 6:1. This is a much lower surfactant to iodine ratio than is generally permissible when using nonionic surfactants; and the ability to use smaller amounts of surfactants is a factor contributing to the extremely low foaming characteristics of the new compositions.

The following examples show in greater detail some preferred cleaning and sanitizing compositions in accordance with the present invention for C-I-P equipment, as well as some significant data on the effect of pH on foaming tendencies of the anionic-amphoteric surfactant mixture; but it is to be understood that these examples are given by way of illustration and not of limitation.

EXAMPLE I

	percent, w./w.	Active anhydrous basis, wt. percent
Component:		
Igepon CN-42 (23% active).....	15.0	3.45
Nacconol NRSF (98% active).....	0.4	0.38
Deriphat 160 (97% active).....	1.0	0.97
HI-I ₂ solution (57% avail. I ₂).....	3.3	1.88
Phosphoric acid (75% active).....	40.0	30.0
Isopropyl alcohol.....	20.0	20.0
Water.....	20.3	
Total.....	100.0	

When tested for foaming at a 1/640 use dilution using the "dynamic" foam test method above described this composition showed the following results:

	Foam, mls.	pH
Diluted in—		
Distilled water.....	40	2.4
F.D.A. 100 p.p.m. hard water.....	6	2.5

This composition is a very effective cleaner-sanitizer for dairy pipelines and the like, eliminating mechanical problems due to foam and rinsing clean without any traces of tarry deposits or discoloration of equipment.

Compositions of quite similar, low foaming character are obtained when the Deriphat 160 is replaced by an equivalent amount of Deriphat 151, 154 or 170C.

EXAMPLE II

Component:	percent, w./w.	Active anhydrous basis, wt. percent
Igepon CN-42 (23% active).....	15.0	3.45
Nacconol NRSF (95% active).....	0.4	0.38
Miranol HM (37% active).....	2.7	1.0
HI-I ₂ solution (57% avail. I ₂).....	3.3	1.88
Phosphoric acid (75% active).....	40.0	30.0
Isopropyl alcohol.....	20.0	20.0
Water.....	18.6	
Total.....	100.0	

When tested for foaming at a 1/640 use dilution using the "dynamic" foam test method above described, this composition showed the following results:

	Foam, mls.	pH
Diluted in—		
Distilled Water.....	50	2.4
F.D.A. 100 p.p.m. hard water.....	14	2.5

The slightly higher foaming than in Example I is of no consequence. This composition is equally effective in cleaning dairy pipelines and other C-I-P equipment.

Compositions of quite similar low foaming character are obtained when the Miranol HM is replaced by an equivalent amount of Miranol CM, DM, SM or DM.

EXAMPLE III

A cleaning-sanitizing composition is prepared containing:

Component:	percent, w./w.	Active anhydrous basis, wt. percent
Igepon CN-42 (23% active).....	15.0	3.45
Nacconol NRSF (95% active).....	0.4	0.38
Miranol HM (37% active).....	5.4	2.0
HI-I ₂ solution (57% avail. I ₂).....	3.3	1.88
Phosphoric acid (75% active).....	40.0	30.0
Isopropyl alcohol.....	20.0	20.0
Water.....	15.9	
Total.....	100.0	

In 1/640 use dilutions this composition has a pH of 2.4–2.5, and when tested for foaming by the "dynamic" foam test method gives substantially the same low foam volumes as in Example II.

EXAMPLE IV

The Igepon CN-42 as employed in Examples I and III is a preferred anionic surfactant for use in the new low foaming compositions, but in order to demonstrate the foam depressing effect as acid pH on other anionics the following comparative data is presented:

Solutions were prepared in distilled water containing 0.01% by weight of anionic surfactant, and other solutions were prepared containing 0.01% anionic surfactant and 0.005% amphoteric surfactant (Deriphat 160) providing a 2:1 anionic: amphoteric ratio. Portions of these solutions were adjusted to pH 2.6 and pH 7 using phosphoric acid, and sodium hydroxide as needed, and 100 ml. quantities of such pH adjusted solutions were placed in 250 ml. stoppered cylinders. These cylinders, clamped several at a time on wooden racks were shaken manually 20 times, and the foam volume read immediately after shaking. (While this type of foam test method is much less sensitive than the "dynamic" foam test method above mentioned, it is nevertheless effective for a quick com-

parison of foaming characteristics.) The comparative values expressed in ml. of foam are tabulated below.

	Ml. foam anionic alone		Ml. foam anionic plus Deriphat-160	
	pH 2.6	pH 7	pH 2.6	pH 7
Anionic component:				
(1) Igepon CN-42.....	34	60	10	60
(2) Igepon T-33.....	110	120	70	150
(3) Igepon TC-42.....	110	100	85	110
(4) Nacconol NRSF.....	110	100	60	130

It is significant to note that in all instances the amphoteric surfactant, while inducing as much or more foam at pH 7, caused a substantial reduction in foam at pH 2.6.

To better visualize the pH transition point comparisons 1 and 4 above were repeated with the anionic-amphoteric mixture at a number of intermediate pH values with the following results:

pH	Igepon CN-42 plus Deriphat 160 foam, ml.	Nacconol NRSF plus Deriphat 160 foam, ml.
	1a	4a
2.6.....	10	60
3.0.....	14	60
4.0.....	55	110
5.0.....	60	120
6.0.....	60	120
7.0.....	60	130

It is apparent from these results that a major change in foaming tendency takes place between pH 3 and pH 4.

In considering the tabulations in this example it should be realized that a system which creates over 60 ml. of foam by the shake method, will overflow the 500 ml. gas washing bottle if tested by the "dynamic" foam test method. Expressed another way, the "dynamic" foam test method provides comparative foaming properties on systems which would show substantially "0" foam by the shake method.

EXAMPLE V

A Cleaning-sanitizing composition is prepared containing:

Component:	Percent, w./w.	Active anhydrous basis, wt. percent
Igepon CN-42 (23% active).....	15.0	3.45
Deriphat 160 (97% active).....	1.0	.97
Phosphoric acid (75% active).....	40.0	30.0
HI-I ₂ solution (57% avail. I ₂).....	3.3	1.88
Propylene glycol.....	10.0	10.0
Water.....	30.7	
Total.....	100.0	

A solution of this composition 1/640 in distilled water showed a pH of 2.4. Separate portions of this solution were adjusted to different pH levels by addition of dilute NaOH solution and 100 ml. portions in 250 ml. stoppered cylinders were shaken to generate foam as described in Example IV, with the following results:

	pH					
	2.5	3.0	3.5	4.0	5.0	6.0
Foam, ml. (Shake method).....	0	0	0	40	40	50
Foam, ml. (Dynamic test).....	40	50	70	>350	(¹)	(¹)

¹ Overflows test cylinders.

This clearly indicates that the advantageous low foaming properties of the new compositions are dependent on providing at use dilution a pH below about 3.5. Furthermore, since accurate check of pH in the field is impractical it is preferable to formulate compositions with sufficient acid to provide a pH below about 3.0 at recommended use dilution in all water normally to be encountered.

7 EXAMPLE VI

A cleaning-sanitizing composition is prepared containing:

Component:	Percent, w/w.	Active anhydrous basis, wt. percent
Igepon CN-42 (23% active).....	15.0	3.45
Deriphat 160 (97% active).....	1.0	0.97
HI-I ₂ solution (57% avail. I ₂).....	3.3	1.88
Hydroxyacetic acid (70% active).....	20.0	14.0
Phosphoric acid (75% active).....	20.0	15.0
Isopropyl alcohol.....	10.0	10.0
Water.....	30.7	
Total.....	100.0	

A 1/640 use dilution of this composition provides a pH of about 2.7 and has low foam characteristics similar to the composition of Example V.

EXAMPLE VII

A cleaning-sanitizing composition is prepared containing:

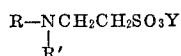
Component:	Percent, w/w.	Active anhydrous basis, wt. percent
Igepon CN-42 (23% active).....	15.0	3.45
Deriphat 160 (97% active).....	1.0	0.97
HI-I ₂ solution (57% avail. I ₂).....	3.3	1.88
Hydroxyacetic acid (70% active).....	40.0	28.0
Isopropyl alcohol.....	5.0	5.0
Water.....	35.7	
Total.....	100.0	

A 1/640 use dilution of this composition provides a pH of about 2.5 and has low foam characteristics similar to the composition of Example V.

Various changes and modification in the low foaming surfactant-iodine compositions herein disclosed will occur to those skilled in the art, and to the extent that such changes and modifications are embraced by the appended claims it is to be understood that they constitute part of the present invention.

We claim:

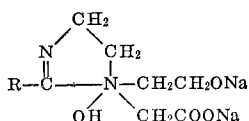
1. A low-foaming surfactant-iodine composition for use in cleaned-in-place equipment, said composition consisting essentially of (a) one part by weight of available iodine, (b) 1 to 4 parts of an anionic surfactant comprising an alkanoyl taurate of the formula:



where R is the radical $\text{C}_x\text{H}_{2x+1}\text{CO}$, being an integer from 11 to 17, R' is selected from the group consisting of hydrogen, lower (C_1 to C_4) alkyl and cyclohexyl radicals, and Y is selected from the group consisting of hydrogen and alkali metal and ammonium cations (c) .25 to 2 parts of an amphoteric surfactant selected from the group consisting of the formula:



wherein R is fatty alkyl, R' is the group $-\text{CH}_2\text{CH}_2\text{COOX}$ wherein X is selected from the group consisting of H and alkali metal and ammonium cations, and R² selected from the class consisting of hydrogen, fatty alkyl and R', and compounds of the formula:



wherein R is a fatty alkyl group containing 9 to 17 car-

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bon atoms, and compounds of the above formula wherein the substituted nitrogen has a single substituent the group $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOX}$ wherein X is selected from the group consisting of hydrogen and alkali metal and ammonium cations, (d) 12 to 50 parts of an acid selected from the group consisting of phosphoric acid, hydroxyacetic acid, and mixtures thereof, and (e) aqueous alcoholic diluent in an amount to provide in said composition an available iodine concentration of about 0.5 to 2.5%.

2. A low-foaming surfactant-iodine composition as defined in claim 1 wherein the proportion of anionic surfactant to amphoteric surfactant is within the range of about 2 to 4 parts anionic surfactant per part by weight of amphoteric surfactant.

3. A low-foaming surfactant-iodine composition as defined in claim 1 wherein the amount of acid is within the range of 15 to 30 parts per part by weight of available iodine.

4. A low-foaming surfactant-iodine composition as defined in claim 1 wherein the anionic surfactant component includes a lesser amount of an alkali metal alkyl aryl sulfonate, wherein the alkyl group contains 6-16 carbon atoms.

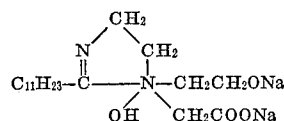
5. A low-foaming surfactant-iodine composition as defined in claim 1 wherein said anionic surfactant also includes a lesser amount of a sulfonate selected from the class consisting of alkali metal C_8 - C_{16} alkyl benzene sulfonates and C_6 - C_{12} alkyl naphthalene sulfonates.

6. A low-foaming surfactant-iodine composition as defined in claim 1 wherein the anionic surfactant is sodium N-cyclohexyl-N-palmitoyl taurate.

7. A low-foaming surfactant iodine composition as defined in claim 1 wherein the anionic surfactant is a mixture of sodium N-cyclohexyl-N-palmitoyl taurate and a lesser amount of sodium dodecylbenzene sulfonate.

8. A low-foaming surfactant-iodine composition as defined in claim 1 wherein the amphoteric surfactant is disodium N-lauryl-B-iminodipropionate.

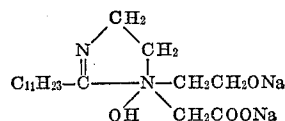
9. A low-foaming surfactant-iodine composition as defined in claim 1 wherein the amphoteric surfactant is a compound of the formula:



10. A low-foaming surfactant-iodine composition as defined in claim 1 wherein the anionic surfactant is sodium N-cyclohexyl-N-palmitoyl taurate, and the amphoteric surfactant is disodium N-lauryl-B-iminodipropionate.

11. A low-foaming surfactant-iodine composition as defined in claim 1 wherein the anionic surfactant is a mixture of sodium N-cyclohexyl-N-palmitoyl taurate and a lesser amount of sodium dodecylbenzene sulfonate, and the amphoteric surfactant is disodium N-lauryl-B-iminodipropionate.

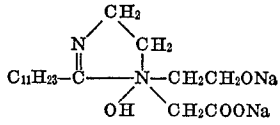
12. A low-foaming surfactant-iodine composition as defined in claim 1 wherein the anionic surfactant is N-cyclohexyl-N-palmitoyl taurate, and the amphoteric surfactant is a compound of the formula



13. A low-foaming surfactant-iodine composition as defined in claim 1 wherein the anionic surfactant is a mixture of N-cyclohexyl-N-palmitoyl taurate and a lesser

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amount of sodium dodecylbenzene sulfonate, and the amphoteric surfactant is a compound of the formula



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