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ANIONIC IODINE COMPLEXES

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This invention relates to new germicidal compositions in which iodine is complexed with certain anionic detergents providing products having unusual iodine stability. More particularly, the invention relates to a new group of germicidal compositions wherein iodine is complexed with anionic detergents of the alkanoyl taurate series in the presence of iodide, and to certain of the compositions within such group which have low foaming characteristics especially adapting them to particular uses.

The developments of the past decade in the field of surface active carrier-iodine complexes have shown that a considerable number of nonionic and cationic surface active agents can be employed as iodine carriers, but that anionic surface active agents are generally not capable of providing stable iodine formulations. One exception to this general observation is found in the alkyl aryl sulfonates, such as alkyl benzene sodium sulfonate and alkyl naphthyl sodium sulfonate, iodine complexes of which are disclosed and claimed in a joint application of one of the present applicants, Serial No. 718,959, issuing March 28, 1961, as United States Patent No. 2,977,278.

It has also been found, and separately disclosed and claimed in a pending application Serial No. 55,732, filed September 13, 1960, of two of the present applicants, that with nonionic and cationic surface active agents which are good complexers of iodine, the firmness of the binding or complexing of iodine is markedly enhanced by a source of iodide (I^-) in excess of about 0.25 part per part of iodine, supplied by HI or an alkali metal iodide. With the anionic alkyl aryl sulfonates, however, the presence of iodide has little effect on the complexing of iodine.

It is now discovered, in accordance with the present invention that a small group of anionic surface active agents, known per se and generally referred to as alkanoyl taurates, will form complexes with iodine which are distinctly superior to the alkyl aryl sulfonate complexes. Furthermore, the alkanoyl taurate-iodine complexes have been found to exhibit markedly enhanced iodine complexing in the presence of a source of iodide (I^-). Indeed, the new alkanoyl taurate-iodine-iodide compositions of the present invention provide for the first time anionic carrier-iodine products which are comparable with the nonionic carrier-iodine products in the area of iodine complexing and stability.

The anonic surface active agents useful in accordance with the present invention are a small and well defined group of alkanoyl taurates which can be represented by the formula:

$$R-\underset{\underset{R'}{|}}{N}-CH_1CH_2SO_3Y$$

wherein R is the radical $C_xH_{2x+1}CO-$, x being an integer

from 5 to 17, R_1 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.

As with other surface active carrier-iodine compositions, the new compositions of the present invention can be prepared in the form of solid formulations or concentrated solutions for dissolving in or dilution with water to provide use solutions which may vary from a few parts per million to several hundred parts per million of iodine depending on the particular use intended. In any such formulations, however, the proportions of carrier, iodine and iodide should fall within certain preferred ranges regardless of the amount of water or other diluent that may be present in a liquid or solid concentrate as intended (as products) for sale and distribution. Practical commercial products may range in iodine content from about 0.05% to 20% iodine, with suitable general purpose products having an iodine content of about 0.5 to 2.5%.

The proportion of alkanoyl taurate to iodine is suitably within the range of about 2 to 1 to about 50 to 1 and preferably within the range of about 5 to 1 to about 20 to 1. The proportion of iodide (I^-) to iodine should be in excess of 0.25:1 and preferably about 0.4:1 to about 5:1 with the further limitation that the amount of iodide should be sufficient to provide a distribution coefficient, D.C. (as hereinafter described) in excess of 25 and preferably in excess of 50. This iodide (I^-) is suitably supplied either by HI or an alkali metal iodide.

Distribution coefficient is a measure of iodine complexation in carrier-iodine compositions which is determined by a method employing a closed equilibrium type system and depending on the equilibrium of iodine between an aqueous solution containing complexing agent or carrier and a non-miscible solvent, heptane. The initial amount of iodine in the aqueous solution is determined by ordinary thiosulfate titration; the final iodine concentration in the heptane is determined colorimetrically; and the amount of iodine remaining in the aqueous phase is then found by difference. Excellent reproducibility is possible, making the procedure a useful tool in evaluating even small differences between similar compositions.

The distribution coefficient (D.C.) as herein employed is determined by adding 1.00 ml of standardized test solution containing between about 0.05 and 5.0% iodine to a 50 ml. graduated cylinder containing 25 mls. of purified n-heptane. The temperature of the heptane is brought to 25±1° C. The cylinder is stoppered and shaken vigorously by hand for one minute during which time the aqueous solution suspends in the heptane as a uniform haze. The solution is then allowed to stand a minute or two, and the temperature adjustment and shaking are repeated. For best results, the solution should settle for an hour, although only a minute or two are necessary if centrifuged.

The amount of iodine in the heptane layer can be determined colorimetrically at 520 mμ, the absorption peak; the relationship between light absorption and iodine concentration in the solvent is linear through the range 1 to 25 mg. per 100 ml. The distribution coefficient is

calculated by the following formula:

$$D.C.=\frac{\text{mg. I remaining in aq. phase}}{\text{mg. I in heptane}}\times\frac{\text{mls. heptane}}{\text{mls. aq. phase}}$$

Using the Beckman colorimeter with 1.00 cm. cells an absorption of 0.142 corresponds with 1.00 mg. iodine extracted by 25 mls. heptane. Values so obtained are readily reproducible to within 10%, and frequently to within 1%.

Preparation of complexes in accordance with the present invention can be effected by simple mixing of the alkanoyl taurate and iodine under anhydrous or aqueous conditions with the iodide source being introduced concurrently or subsequent to the combining of the iodine and carrier. There is special advantage, however, in adding the desired amount of carrier to an aqueous iodine medium providing a source of iodide (I^-) in excess of about 0.25 part per part of of iodine. In this way, a stable product can be readily obtained without heating or ageing.

In adapting compositions in accordance with the present invention to special uses, it is sometimes desirable to incorporate other acidic and/or surface active components. Thus, for example, germicidal formulations intended for use in the dairy or food handling industries, or in other areas where large amounts of organic soil are encountered, should preferably contain an acid, such as phosphoric acid or hydroxyacetic acid in an amount sufficient to provide a pH below about 4, and suitably about pH 3 in the intended use dilution. For this purpose, the amount of acid may be as high as 50 to 60% by weight of the formulation.

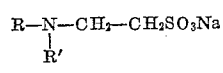
Special problems also arise in the germicidal cleaning of equipment and pipelines used in certain food handling industries, and particularly in the dairy industry due to the normal foaming tendencies of surface active carrier-iodine formulations. It has been found that compositions in accordance with the present invention, and particularly those containing an octanoyl-substituted taurate as carrier, can provide low foaming properties especially adapting them for such uses. The optimum low foaming characteristics are achieved when the product contains a small amount, i.e. 15 to 50% of the weight of the iodine present, of a nonionic surface active agent which can be described as a nonylphenol ethylene oxide condensate containing about 1.5 mols of ethylene oxide per mol of nonyl phenol. This material, although itself water insoluble, goes into solution in the iodine formulation providing a stable product, and one which is unique in its low foaming properties while retaining good detergent and excellent germicidal properties.

The following examples will provide a better understanding of typical germicidal compositions in accordance with the present invention, but it is to be understood that these examples are given by way of illustration and not of limitation.

Example I

A group of alkanoyl taurate-iodine compositions were prepared containing 10% by weight of the alkanoyl taurate and approximately 1% of iodine in aqueous solution with varied amounts of iodide supplied by HI. These compositions have a concentration of iodine adapting them for use as general purpose germicidal products (for distribution and sale).

The variation in the structure of the alkanoyl taurates will be understood from the formula:



and the identification of the substituents R and R′ in the following tabulation. For each of the different taurates employed distribution coefficient, D.C., values, determined as above described, are given at four different iodide (I^-) concentrations as identified in the table:

	Carrier		Percent Titratable Iodine	0.4	1.0	2.0	4.0
	R	R′					
a	$C_5H_{11}CO$	CH_3	1.5	18	39	73	131
b	$C_7H_{15}CO$	H	1.00	11	22	44	48
c	do	CH_3	1.06	41	90	194	405
d	do	cyclo hexyl.	1.1	98	140	191	347
e	$C_{11}H_{23}CO$	CH_3	1.1	46	100	178	440
f	do	CH_3CH_2	1.14	43	100	144	303
g	do	cyclo-hexyl.	0.93	61	90	111	190
h	$C_{13}H_{27}CO$	CH_3	1.05	22	28	60	105
i	$C_{17}H_{33}CO$	CH_3	(1)				

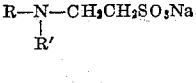
[1] With respect to item *i* the solubility of the carrier and the resulting iodine-iodide complexes was too low to permit comparison under the test conditions (10% carrier and approximately 1% iodine in aqueous solution). These complexes are suitable, however, for use in aqueous products containing 1% carrier and about 0.1% iodine (practical for certain types of germicidal products), as well as in solid products intended for preparation of use solutions containing less than 0.1% iodine.

Bearing in mind that a product, to be of high quality from the standpoint of iodine stability, if it is to be stored as an aqueous solution, must have a distribution coefficient in excess of 25, and preferably in excess of 50, it is evident that with proper selection of the amount of iodide, all of the compositions containing alkanoyl taurate carriers provide high quality products.

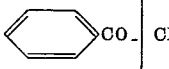
Example II

A number of alkanoyl taurate-iodine compositions were prepared representative of products for use in food handling industries, i.e. containing phosphoric acid, and in some instances also containing as anti-foaming agent a nonyl phenol ethylene oxide condensate containing about 1.5 mols of ethylene oxide per mol of nonyl phenol. These compositions were prepared by dissolving the indicated amount of iodine in an aqueous solution of the taurate, and then adding the phosphoric acid and anti-foam agent. All of the compositions were found to be stable at room temperature and at 125° F. for a period of at least two weeks. All were tested for foaming characteristics as determined by a newly devised "dynamic" foam test method at dilutions which provides a 25 p.p.m. iodine concentration. In this method 150 ml. of the solution to be tested 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 reached at a temperature of 25° C. Foam values of 50 to 75 cc. represent preferred formulations for pipeline and equipment cleaning and other uses when low foaming is important, although even formulations having foam values as high as 125 are considered low foam products. All of the compositions were also tested by the method hereinabove described to determine distribution coefficient (D.C.).

The result are tabulated below with the various taurates being identified with reference to the following formula:



and the changes in the substituents R and R′ as noted in the table. All percentages are by weight based on the weight of the complete formulation:

	Carrier		Percent	Percent I_2	Percent H_3PO_4	Percent Anti-Foam	Foam, cc.	D.C.
	R	R'						
a	$C_7H_{15}CO$	H	6	1.5	56	0.35	65	33.8
b	$C_7H_{15}CO$	H	6	1.5	56		150	30.2
c	$C_7H_{15}CO$	H	5	1.5	56	0.35	50	26.2
d		CH_3	9	1.5	30		30	20
e	$C_5H_{11}CO$	CH_3	6	1.5	30		160	19
f	$C_7H_{15}CO$	CH_3	4	0.5	30	0.15	50	19
g	$C_7H_{15}CO$	CH_3	6	0.5	30	0.15	100	30
h	$C_7H_{15}CO$	CH_3	6	0.5	30	0.25	70	31
i	$C_7H_{15}CO$	CH_3	4	1.5	30	0.25	60	30
j	$C_7H_{15}CO$	CH_3	5	1.5	30	0.25	65	37
k	$C_7H_{15}CO$	CH_3	6	1.5	30	0.25	80	53
l	$C_7H_{15}CO$	CH_3	10	1.5	30	0.6	60	78
m	$C_7H_{15}CO$	CH_3	6	1.5	30		160	47
n	$C_7H_{15}CO$	CH_3	6	1.5	56	0.35	60	52
o	$C_7H_{15}CO$	CH_3CH_2	6	1.5	30	0.25	80	47.7

It will be understood that the foregoing table shows D.C. values for he formulations without iodide. Addition of iodide provide a marked increase in D.C. values (and iodine stability) in the manner indicated in Example I. The following example will illustrate the typical effect of added iodide in such complex formulations.

Example III

Three formulations similar to those in Example II were prepared using differing amounts of iodide added as HI and the comparative distribution coefficients determined. The pertinent data and results are tabulated below, amounts of components being expressed in parts by weight:

	Formulations		
	a	b	c
N-methyl-n-octanoyl sodium taurate (20% aqueous sol.)	30	30	30
HI (40% aqueous sol.)	1.65	3.3	4.95
Iodine	1.65	1.65	1.65
H_3PO_4 (85%)	66.35	64.7	63.05
Nonyl phenol ethylene oxide (1.5:1 eth. ox.: phenol)	0.35	0.35	0.35
HI/I_2 ratio	1:2	1:1	1.5:1
D.C.	46.0	81.4	115.2

Various changes and modifications in the alkanoyl taurate-iodine complexes of the present invention and the utilization thereof in special purpose formulations 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 our invention.

We claim:

1. A germicidal composition comprising a complex of iodine with an alkanoyl taurate of the formula:

$$R{-}N(R'){-}CH_2CH_2SO_3Y$$

wherein R is a radical of the formula $C_xH_{2x+1}CO$ with 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, the proportion of alkanoyl taurate to iodine being within the range of about 2:1 to 50:1 and preferably about 5:1 to 20:1.

2. A germicidal composition as defined in claim 1 wherein the amount of iodine present is between about 0.05% and 20%.

3. A germicidal composition as defined in claim 1 wherein the amount of iodine present is about .5–2.5%.

4. A germicidal composition as defined in claim 3 wherein the alkanoyl taurate is an n-octanoyl-substituted taurate.

5. A germicidal composition as defined in claim 1 wherein Y is sodium.

6. A germicidal composition as defined in claim 1 containing an iodide selected from the group consisting of HI and alkali metal iodides in an amount to provide an iodide: iodine ratio in excess of about 0.25:1 and sufficient to provide a distribution coefficient in excess of about 25 as determined by the equation:

$$D.C.=\frac{\text{mg. I in aqueous ph.}}{\text{mg. I in heptane}}\times\frac{\text{ml. heptane}}{\text{ml. aq. phase}}$$

7. A germicidal composition as defined in claim 6 wherein the iodide:iodine ratio is within the range of about 0.4:1 to 5:1.

8. A germicidal composition as defined in claim 1 containing an amount of an acid selected from the group consisting of phosphoric acid, hydroxyacetic acid and mixtures thereof sufficient to provide a pH below about 4 in intended use dilutions of such composition, and further containing an amount, within the range of about 15 to 50% based on the weight of the iodine present, of a nonylphenol ethylene oxide condensate having about 1.5 mols of ethylene oxide per mol of nonylphenol.

9. A germicidal composition as defined in claim 8 containing an iodide selected from the group consisting of HI and alkali metal iodides in an amount to provide an iodide:iodine ratio in excess of about 0.25:1 and sufficient to provide a distribution coefficient in excess of about 25 as determined by the equation:

$$D.C.=\frac{\text{mg. I in aqueous ph.}}{\text{mg. I in heptane}}\times\frac{\text{ml. heptane}}{\text{ml. aq. phase}}$$

10. A germicidal composition as defined in claim 9 wherein the iodide:iodine ratio is within the range of about 0.4:1 to 5:1.

11. A germicidal composition as defined in any of claims 8, 9 and 10 wherein the alkanoyl taurate is an n-octanoyl-substituted taurate, whereby said composition possesses extremely low foaming properties.

12. A germicidal composition comprising a complex of iodine with N-methyl-n-octanoyl sodium taurate, the proportion of said taurate to iodine being within the range of 2:1 to 50:1 and preferably about 5:1 to 20:1.

13. A germicidal composition as defined in claim 12 wherein the amount of iodine present is about 0.5 to 2.5% of said composition.

14. A germicidal composition as defined in claim 12 containing an iodide selected from the group consisting of HI and alkali metal iodides in an amount to provide proportions of iodide (I^-) to iodine within the range of about 0.4:1 to 5:1.

15. A germicidal composition as defined in any of claims 12 to 14 containing an amount of an acid selected from the group consisting of phosphoric acid, hydroxyacetic acid, and mixtures thereof to provide a pH below about 4 in intended use dilutions of such composition, and further containing an amount, within the range of about 15 to 50% based on the weight of the iodine present, of

a nonylphenol ethylene oxide condensate having about 1.5 mols of ethylene oxide per mol of nonylphenol.

16. A germicidal composition comprising a complex of iodine with N-methyl-n-dodecanoyl sodium taurate, the proportion of said taurate to iodine being within the range of 2:1 to 50:1, and preferably about 5:1 to 20:1.

17. A germicidal composition comprising a complex of iodine with N-cyclohexyl-n-octanoyl sodium taurate, the proportion of said taurate to iodine being within the range of 2:1 to 50:1, and preferably about 5:1 to 20:1.

18. A germicidal composition comprising a complex of iodine with N-ethyl-n-octanoyl sodium taurate, the proportion of said taurate to iodine being within the range of 2:1 to 50:1, and preferably about 5:1 to 20:1.

19. A germicidal composition comprising a complex of iodine with N-ethyl-n-dodecanoyl sodium taurate, the proportion of said taurate to iodine being within the range of 2:1 to 50:1, and preferably about 5:1 to 20:1.

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