

Controlled Foam Aqueous Quaternary Ammonium and Phosphonium Compositions

This invention relates to a method for controlling foam formation in aqueous systems containing biocidal quaternary ammonium and/or phosphonium compounds ("quats"). This invention also relates to low foam aqueous formulations comprising quaternary ammonium and/or phosphonium compounds and the use of said formulations compounds in a method for killing or inhibiting the growth of microorganisms, algae and fungi.

Several quaternary ammonium and phosphonium compounds ("quats") exhibit marked biocidal activity and, consequently, have been used as active ingredients in disinfectants, preservatives, or other compositions for killing or controlling the growth of microorganisms, such as bacteria or viruses, as well as algae and fungi for many years. However, since many of those quats have also surfactant properties, their use in aqueous systems is often impaired by intensive foaming even at low quat concentrations in the ppm range, which is particularly detrimental in applications where aqueous systems are agitated while being exposed to the atmosphere, such as swimming pool or spa waters or waters in cooling towers.

The problem to be solved by the present invention was to provide a method for the suppression of foaming in aqueous systems containing at least one biocidal quat.

According to the invention, the problem has been solved by the method of claim 1. Applicants have found that the addition of at least one anionic surfactant to an aqueous system containing at least one biocidal quaternary ammonium and/or phosphonium compound in an amount corresponding to a molar ratio of anionic surfactant to quaternary ammonium and/or phosphonium compound of from 0.001 to 0.2 (i.e., 0.001:1 to 0.2:1), preferably from 0.001 to 0.09, substantially reduces the volume and lifetime of foam formed during the use of the aqueous system.

As anionic surfactants are known to decrease the biocidal efficacy of quaternary ammonium compounds, the observed foam reduction achieved by addition of anionic surfactants at much less than a molar equivalency is important from the quat performance perspective. Since only small amounts of e.g. 0.1 or 0.02 molar equivalents of anionic surfactant are required, the compositions retain about 90 or 98 percent, respectively, of their active quat concentrations.

In a more preferred embodiment, the molar ratio of anionic surfactant to quaternary ammonium and/or phosphonium compound is from 0.001 to 0.05.

Preferably, the at least one quaternary ammonium and/or phosphonium compound is selected from

- (i) a compound having the formula $[QR^1R^2R^3R^4]^+ X^-$ (I), wherein Q is nitrogen or phosphorus, R^1 and R^2 are independently unsubstituted or hydroxy-substituted linear or branched C_{1-4} alkyl; $-(CH_2CH_2O)_mCH_2CH_2OH$, or $-(CH_2CH(CH_3)O)_mCH_2CH(CH_3)OH$, where m in each molecule independently is an integer from 1 to 10;
 R^3 is an optionally substituted benzyl, ethylbenzyl, naphthylmethyl, or linear or branched C_{6-22} alkyl group;
 R^4 is an optionally substituted benzyl, ethylbenzyl, methylnaphthyl, or linear or branched C_{1-22} alkyl group or $-R^5(O)_n(C_6H_4)R^6$, wherein n is 0 or 1;
 R^5 is substituted or unsubstituted C_{1-8} alkanediyl or $-(CH_2)_p-O-(CH_2)_q-$ wherein p and q independently are integers from 1 to 8;
 R^6 is hydrogen or a substituted or unsubstituted, linear or branched C_{1-12} alkyl group; and X^- is a monovalent or one equivalent of a polyvalent anion;
- (ii) a compound having the formula $R^{19}R^{20}R^{21}R^{22}Q^+X^-$ (II), wherein Q is nitrogen or phosphorus, R^{19} , R^{20} , R^{21} , and R^{22} are independently linear, branched, cyclic or any combination thereof saturated or unsaturated hydrocarbyl groups, X^- is a monovalent or one equivalent of a polyvalent anion, and the sum of the carbon atoms numbers of R^{19} , R^{20} , R^{21} and R^{22} ranges from 10 to 50;
- (iii) a polymeric quaternary ammonium or phosphonium biocide; and
- (iv) a mixture of two or more quaternary compounds of any of (i) to (iii).

More preferably, the quaternary ammonium and/or phosphonium compound has the formula $[QR^1R^2R^3R^4]^+ X^-$ (I), wherein Q is as defined above, both R^1 and R^2 are C_{1-4} alkyl, R^3 is a linear or branched C_{6-22} alkyl, R^4 is benzyl or a linear or branched C_{1-22} alkyl and X^- is chloride.

Still more preferably, the quaternary ammonium and/or phosphonium compound has the formula $[QR^1R^2R^3R^4]^+ X^-$ (I), wherein Q is as defined above, both R^1 and R^2 are methyl, R^3 is a linear or branched C_{6-22} alkyl, R^4 is benzyl or a linear or branched C_{6-22} alkyl and X^- is chloride.

Most preferably, Q is nitrogen.

Particularly preferred are ammonium and phosphonium compounds such as alkyldimethylbenzylammonium chloride or tributyl-tetradecylphosphonium chloride.

In another preferred embodiment, X^- in formula (I) and/or (II) is selected from the group consisting of $\frac{1}{2}\text{CO}_3^{2-}$, HCO_3^- and OH^- .

In still another preferred embodiment the at least one anionic surfactant is a sulfonate.

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In another preferred embodiment the at least one anionic surfactant is a diester.

In a particularly preferred embodiment, the at least one anionic surfactant is selected from the group consisting of diamyl sulfosuccinate, dihexyl sulfosuccinate, dioctyl sulfosuccinate, diti-
10 decyl sulfosuccinate, the potassium, sodium and calcium salts of any of the foregoing and any mixture of any of the foregoing sulfosuccinates and salts.

In one most preferred embodiment, the at least one anionic surfactant is selected from the group consisting of dihexyl sulfosuccinate and the potassium, sodium and calcium salts thereof
15 sulfonate.

In another most preferred embodiment, the at least one anionic surfactant is selected from the group consisting of dioctyl sulfosuccinate and the potassium, sodium and calcium salts thereof.

20 In still another most preferred embodiment, the at least one anionic surfactant is selected from the group consisting of diamyl sulfosuccinate and the potassium, sodium and calcium salts thereof.

Of the above sulfosuccinate salts, the sodium salts are particularly preferred.

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The above sulfonates have been observed to substantially reduce foaming while maintaining a high level of quat activity.

Preferably, the aqueous system contains from 0.1 to 100 ppm, more preferably from 0.5 to
30 50 ppm, of the biocidal quaternary ammonium and/or phosphonium compound.

Another object of the invention is a low foam formulation comprising at least one biocidal quaternary ammonium and/or phosphonium compound and at least one anionic surfactant, wherein the molar ratio of anionic surfactant(s) to quaternary ammonium and/or phosphonium
35 compound(s) is from 0.001 to 0.2, preferably from 0.001 to 0.09 and more preferably from 0.001 to 0.05.

Preferably, the low foam formulation comprises 5 to 80 wt.%, more preferably 10 to 50 wt.%, based on 100 wt.% total formulation, of the at least one biocidal quaternary ammonium and/or phosphonium compound.

- 5 The low foam formulations of the present invention are stable single phase clear solutions.

Preferably the low foam formulation contains at least one performance additive such as a dye or perfume.

- 10 Still another object of the invention is a method for killing or inhibiting the growth of microorganisms, zooplankton, algae and/or fungi comprising applying the above formulations to an aqueous system or to a porous or hard surface.

In a preferred embodiment the porous or hard surface is wood, metal or plastic.

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In another preferred embodiment the formulation is used as a wood preservative.

In still another preferred embodiment the formulation is used as a disinfectant or sanitizer for hard surfaces.

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In yet another preferred embodiment the aqueous system is selected from the group consisting of cooling waters, waste waters, waters used on oil fields for injection, test or recovery purposes, recreational pool or spa waters, ballast water, and pulp or papermaking slurries.

- 25 Most preferably, the aqueous system is cooling water, ballast water or recreational pool or spa water.

Particularly preferred is the application as algacides in pool or spa waters.

- 30 Preferably, the aqueous system contains from 0.1 to 100 ppm, preferably from 0.5 to 50 ppm, of the biocidal quaternary ammonium and/or phosphonium compound.

The invention is further illustrated by the following non-limiting examples.

35 **Examples**

Method:

Test solutions were prepared from the selected quaternary ammonium compounds and the selected anionic surfactants in 20 °C tap water (pH = 7-8, Total Hardness = 160-300 ppm as

CaCO₃ and Total Alkalinity = 150–250 ppm as CaCO₃). 150 mL of each test solution was added to a 250 mL stoppered graduated mixing cylinder, the solution was agitated by inverting the cylinder ten times and the foam volume measured immediately after agitation and again after 30 seconds settling time. Also measured was the time for total collapse of the foam (“time to no foam”). All quat concentrations in ppm or percent are on a weight basis and refer to the actual content of active ingredient, unless otherwise indicated.

Example 1 (Reference Example)

An alkyl (67% C₁₂, 25% C₁₄, 7% C₁₆, 1% C_{8,10,18}) dimethylbenzylammonium chloride (ADBAC; Barquat[®] 50-65B, Lonza Inc., Allendale, NJ) was selected as a representative quaternary ammonium compound for foam evaluation. As shown in Table 1 below, ADBAC produced a substantial amount of foam, generating an initial foam volume of 25 mL and maintaining 10 mL of foam after 30 seconds. As a comparison, the foaming behavior of the polymeric quat poly[oxyethylene(dimethyliminio)ethylene(dimethyliminio)ethylene dichloride] (WSCP; Buckman Laboratories International, Inc., Memphis, TN) was also tested.

Example 2

The effect of the anionic surfactant sodium dioctyl sulfosuccinate (NaDOSS) on ADBAC foaming was determined as described above. The results are shown in Table 1 below. The addition of only a 0.1 molar equivalent of NaDOSS relative to the active quat reduced the initial foam volumes by 85 percent from 25 mL to 4 mL. Even the application of only a 0.02 molar equivalent of NaDOSS resulted in merely 6 mL initial foam volume and complete foam loss within 10 seconds.

Example 3

The ability of NaDOSS to control foam at low concentrations of quaternary ammonium compounds, as they are frequently utilized in water treatment applications such as swimming pool algicides, was tested at quat concentrations of 2 ppm using the methodology of Example 2. For comparison purposes one test was performed without addition of NaDOSS. The results are shown in Table 1 below. It has been found that NaDOSS concentrations as low as 0.05 ppm can control foaming at 2 ppm quat concentration.

Example 4

The alternative anionic surfactants sodium dihexyl sulfosuccinate (NaDHSS) and sodium dodecyl sulfosuccinate (NaDTSS) were also tested as foam reducing agents using the methodology of Example 2. The results are shown in Table 1 below. It has been found that NaDHSS concentrations as low as 1.1 ppm controlled foaming of 10 ppm quat (corresponding to a molar ratio of anionic surfactant to quat of 0.10) while concentrations as low as 0.2 ppm still showed a

small effect. Similar results have been obtained with NaDTSS at concentrations of 1.7 ppm (corresponding to a molar ratio of anionic surfactant to quat of 0.10) and 0.4 ppm, respectively. NaDHSS was preferred as it produced clear solutions at all tested concentrations.

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Table 1

Example No.	Quat		Sulfonate		Sulfonate/Quat Molar Ratio	Foam Volume [mL]		Time to No Foam [s]
	Type	Amount [ppm]	Type	Amount [ppm]		Initial	30 s	
1	50-65B	10	—	—	0	25	10	>30
1	WSCP	10	—	—	0	0	0	<1
2	50-65B	10	NaDOSS	1.3	0.1	4	0	5
2	50-65B	10	NaDOSS	0.26	0.02	6	0	10
3	50-65B	2	—	—	0	20	0	20
3	50-65B	2	NaDOSS	0.05	0.02	10	0	5
4	50-65B	10	NaDHSS	1.1	0.1	10	0	8
4	50-65B	10	NaDHSS	0.2	0.02	20	4	>30
4	50-65B	10	NaDTSS	1.7	0.1	10	0	4
4	50-65B	10	NaDTSS	0.4	0.02	20	2	>30

Example 5

As shown in the preceding examples, NaDOSS can be applied separately to quat-containing solutions to achieve the desired foam reduction. However, for practical reasons, in particular ease of application, it is desirable to provide single formulations (concentrates) containing the quats and the anionic surfactants in an optimized molar ratio. Therefore the phase stability of two formulations containing Barquat® 50-65B and NaDOSS was tested. The results are shown in Table 2 below.

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Table 2

NaDOSS/Quat Molar Ratio	Quat Content [%]	NaDOSS Content [%]	Appearance
0.02	49.2	1.2	Single phase, clear
0.10	46.1	5.8	Single phase, clear

It has been found that clear phase-stable formulations containing NaDOSS and ADBAC in molar ratios of 0.02 and 0.10 can be prepared. Test solutions with 10 ppm quat were prepared from these formulations and showed essentially the same foaming behavior as those of Example 2.

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Example 6

Sodium dioctyl sulfosuccinate (NaDOSS) and sodium dihexyl sulfosuccinate (NaDHSS) were tested in a dynamic recirculation foam test designed to simulate cooling applications. The dynamic foam test consisted of recirculating a 1.5 liter water sample through a large graduated cylinder at a flow rate of 5.7 liter/min (1.5 GPM). The water conditions were: total hardness (as CaCO₃) 280 ppm, total alkalinity (as CaCO₃) 164 ppm, temperature 22 C, and pH = 7.3. Master solutions of the test formulations were added as necessary to achieve the reported concentrations. The results are compiled in Table 3 below.

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Table 3

Sample	Stabilized Foam Height After 5 Minutes (cm)
LF	7.25–8.0
LF + 0.02 mol NaDOSS	4.0
LF + 0.02 mol NaDHSS	6.0

Both tested compounds significantly reduced the foaming properties of 90 ppm active dioctyldimethylammonium chloride (Bardac[®] LF 18, Lonza Inc.). As shown in Table 3, the addition of NaDOSS at a molar ratio (sulfosuccinate/Bardac[®] LF 18) of 0.02 provided a 50% foam reduction, from 8 cm to 4 cm, while addition of NaDHSS at the same molar ratio provided a 25% foam reduction.

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Example 7

The phase stability of two formulations containing Bardac[®] LF 18 and NaDOSS were tested. As shown in Table 4 below, formulations containing NaDOSS at molar ratios of 0.02 and 0.05 are compatible, providing clear, single phase solutions.

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Table 4

NaDOSS/Quat Molar Ratio	Quat Content [%]	NaDOSS Content [%]	Appearance
0.02	51.0	1.5	Single phase, clear
0.05	50.0	3.6	Single phase, clear

Claims

1. A method for controlling foam formation in an aqueous system containing at least one biocidal quaternary ammonium and/or phosphonium compound, said method comprising the addition of at least one anionic diester surfactant in a molar ratio of anionic diester surfactant to quaternary ammonium and/or phosphonium compound of from 0.001 to 0.09, to said aqueous system.
2. The method of Claim 1, wherein the molar ratio of anionic diester surfactant to quaternary ammonium and/or phosphonium compound is from 0.001 to 0.05.
3. The method of Claim 1 or Claim 2, wherein the at least one quaternary ammonium and/or phosphonium compound is selected from
 - (i) a compound having the formula $[QR^1R^2R^3R^4]^+ X^-$ (I), wherein Q is nitrogen or phosphorus;

R^1 and R^2 are independently unsubstituted or hydroxy-substituted linear or branched C_{1-4} alkyl; $-(CH_2CH_2O)_mCH_2CH_2OH$, or $-(CH_2CH(CH_3)O)_mCH_2CH(CH_3)OH$, where m in each molecule independently is an integer from 1 to 10;

R^3 is an optionally substituted benzyl, ethylbenzyl, naphthylmethyl, or linear or branched C_{6-22} alkyl;

R^4 is an optionally substituted benzyl, ethylbenzyl, methylnaphthyl, or linear or branched C_{1-22} alkyl or $-R^5(O)_n(C_6H_4)R^6$, wherein n is 0 or 1 ;

R^5 is substituted or unsubstituted C_{1-8} alkanediyl or $-(CH_2)_p-O-(CH_2)_q-$ wherein p and q independently are integers from 1 to 8;

R^6 is hydrogen or a substituted or unsubstituted, linear or branched C_{1-12} alkyl;

and X^- is a monovalent or one equivalent of a polyvalent anion;
 - (ii) a compound having the formula $R^{19}R^{20}R^{21}R^{22}Q^+X^-$ (II), wherein Q is as defined above, R^{19} , R^{20} , R^{21} , and R^{22} are independently linear, branched, cyclic or any combination thereof saturated or unsaturated hydrocarbyl groups, X^- is a monovalent or one equivalent of a polyvalent anion, and the sum of the carbon atoms numbers of R^{19} , R^{20} , R^{21} and R^{22} ranges from 10 to 50;
 - (iii) a polymeric quaternary ammonium or phosphonium biocide; and
 - (iv) a mixture of two or more quaternary compounds of any of (i) to (iii).

4. The method of Claim 3, wherein the quaternary compound has the formula $[QR_1R_2R_3R_4]^+X^-$, Q is as defined in Claim 3, both R_1 and R_2 are C 1-4 alkyl, R_3 is a linear or branched C6-22 alkyl, R_4 is benzyl or a linear or branched C1-22 alkyl and X^- is chloride.
5. The method of Claim 3 or 4, wherein X^- is selected from the group consisting of $\frac{1}{2}CO_3^{2-}$, HCO_3^- and OH^- .
6. The method of any of Claims 1 to 5, wherein the at least one anionic diester surfactant is a sulfonate.
7. The method of Claims 6, wherein the at least one anionic diester surfactant is selected from the group consisting of diamyl sulfosuccinate, dihexyl sulfosuccinate, dioctyl sulfosuccinate, ditridecyl sulfosuccinate, the potassium, sodium and calcium salts of any of the foregoing, and any mixture of any of the foregoing sulfosuccinates and salts.
8. The method of Claim 7, wherein the at least one anionic diester surfactant is selected from the group consisting of dihexyl sulfosuccinate and the potassium, sodium and calcium salts thereof.
9. The method of Claim 7, wherein the at least one anionic diester surfactant is selected from the group consisting of dioctyl sulfosuccinate and the potassium, sodium and calcium salts thereof.
10. The method of any of Claims 1 to 9, wherein the aqueous system contains from 0.1 to 100 ppm, of the biocidal quaternary ammonium and/or phosphonium compound.
11. A single-phase liquid low foam formulation comprising at least one biocidal quaternary ammonium compound and at least one anionic diester surfactant, wherein the molar ratio of anionic diester surfactant(s) to quaternary ammonium compound(s) is from 0.001 to 0.09.
12. The formulation of Claim 11 comprising 5 to 80 wt.%, based on 100 wt.% total formulation, of the at least one biocidal quaternary ammonium and/or phosphonium compound.
13. The formulation of Claim 1 or Claim 12 containing a dye or perfume or other performance additive.
14. A method for killing or inhibiting the growth of microorganisms, algae and/or fungi, said method comprising applying the formulation of any of Claims 11 to 13 to an aqueous system or to a porous or hard surface.
15. The method of Claim 14, wherein the porous or hard surface is wood, metal or plastic.
16. The method of Claim 15, wherein the formulation is used as a wood preservative.

17. The method of Claim 14, wherein the formulation is used as a disinfectant or sanitizer for hard surfaces.
18. The method of Claim 14, wherein the aqueous system is selected from the group consisting of cooling waters, waste waters, waters used on oil fields for injection, test or recovery purposes, recreational pool or spa waters, ballast water, and pulp or paper- making slurries.
19. The method of Claim 18, wherein the aqueous system is cooling water, ballast water or recreational pool or spa water.
20. The method of Claim 18 or 19, wherein the aqueous system contains from 0.1 to 100 ppm, of the biocidal quaternary ammonium and/or phosphonium compound.