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3,078,236  
PROCESS ANTIFOAMS

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The present invention is directed to methods and compositions for controlling the foaming tendencies of aqueous solutions under various conditions. The invention has particular applicability to the control of foaming in the generation of steam from boiler water under various conditions of pressure.

The present invention is directed to the prevention of foaming, or its control, by the addition of materials to an aqueous system to prevent initiation of foaming conditions and also to the introduction of the compounds into a system already foaming for the purpose of destroying or controlling the foaming condition.

The problems encountered under conditions of boiling under atmospheric pressure, sub-atmospheric pressure, and super-atmospheric pressure may be considerably different insofar as the selection of a suitable anti-foam agent is concerned. Some materials have little or no anti-foam activity at atmospheric pressure or sub-atmospheric pressure, but become extremely effective anti-foams when the boiler is operated at a super-atmospheric pressure. Conversely, some materials are effective anti-foam agents at low pressures but lose their effectiveness when the steam generating system is operated at elevated pressures. With the compositions employed in the practice of the present invention, however, one can select particular compositions for particular pressure conditions and thereby provide an anti-foam which is tailor made for the particular environment.

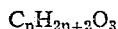
An object of the present invention is to provide an improved method for controlling or inhibiting foam formation in aqueous systems having a tendency to foam.

Another object of the invention is to provide an improved method for destroying existing foaming conditions in aqueous systems.

A further object of the invention is to provide a method for controlling foaming conditions in aqueous systems operating to generate steam under various pressure conditions.

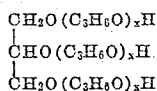
A further object of the invention is to provide an improved self-emulsifiable anti-foam composition for combating foaming tendencies in steam generating systems.

In the practice of the present invention, I employ, as the effective anti-foam agent, a polyoxypropylene addition product of a trihydroxy substituted propane having the empirical formula:



where  $n$  is either 3 or 6.

One class of compounds coming under this definition consists of 1, 2, 3 polyoxypropylene glycerols having the following formula:



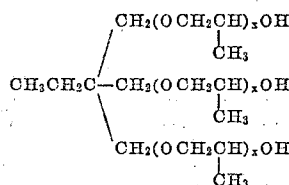
Compounds of the type illustrated in the foregoing

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formula commence exhibiting anti-foam activity at a minimum molecular weight of about 1000, and particularly effective in materials at molecular weights within the range of 1000 to 5000. These addition products are sold commercially by the Dow Chemical Company under the designation "Polyglycol 11." The representative members of this group of compounds are given in the following table:

Compound:	Molecular weight
Polyglycol 11-100	1030
Polyglycol 11-200	2700
Polyglycol 11-300	4000
Polyglycol 11-400	4900

Another class of materials which fall within the class definition are the polyoxypropylene derivatives of trimethylolpropane having the structural formula:



In this type of compound, foam inhibiting effectiveness seems to occur at a minimum molecular weight of 400, and the preferred compounds have molecular weights of from 400 to 5000.

The applicability of the materials as foam destroyers under atmospheric boiling conditions was determined in the following manner. The liquid under test was admitted to a large Pyrex tube and kept at a constant level within the tube by using an inverted flask filled with distilled water. The material was heated by an electrical heating element operating at a constant voltage. The heating element was turned on and the liquid was heated for 40 minutes to reach the constant maximum foam height. Testing material was then added to the boiling liquid. The liquid was heated for another 5 minutes to assure uniform distribution of the testing material within the liquid. The height of foam produced was then measured during a period of 5 minutes. The foam height was recorded as a difference between the average height attained by the liquid plus foam and the original height of the liquid. A slightly alkaline feed water having a pH of 11.0 was used in the test. The following table compares the results obtained from the various compounds employed in the present invention:

Additive	Dosage, percent	Height of foam produced in mm. at specified time intervals				
		1 Min.	2 Min.	3 Min.	4 Min.	5 Min.
Blank		570	580	575	550	572
Polyglycol 11-100	0.037	105	101	108	118	118
Polyglycol 11-200	0.037	258	232	221	201	213
Polyglycol 11-300	0.037	290	262	255	244	236
Polyglycol 11-400	0.037	392	355	362	350	311

The foam controlling effectiveness of these compounds is even further increased when they are combined with

a relatively minor amount of a quaternary ammonium salt having at least 1 hydrocarbon chain containing at least 12 carbon atoms. This effect is particularly surprising since the quaternary salts themselves have little foam inhibiting capability. Suitable quaternary salts for the practice of this invention include materials such as "Arquad 2C" (di-coconut dimethyl ammonium chloride), "Arquad T" (mono-tallow trimethyl ammonium chloride) and "Arquad O" (mono-octadecenyl trimethyl ammonium chloride). These salts, when added in a mixture with the foam inhibiting material to the extent of 5 to 20% of the mixture provide a self-emulsifiable composition which is quite stable.

Under the same conditions of anti-foam testing mentioned previously, the following results were obtained:

Additive	Dosage, percent	Height of foam produced in mm. at specified time intervals				
		1 Min.	2 Min.	3 Min.	4 Min.	5 Min.
90% Polyglycol 11-100 plus 10% Arquad 2C (75% active)	0.037	40	33	35	40	38

While the composition illustrated in the foregoing table is very effective as an anti-foam at atmospheric pressure, when elevated pressures are to be encountered, it is advisable to use a polyoxypropylene glycerol having a higher molecular weight. Particularly good results have been obtained by using the combination of "Polyglycol 11-200" in an amount of 90%, combined with 10% of "Arquad 2C" (75% active). This particular composition evidenced an anti-foam life of 11 minutes and 8 seconds at a dosage of 0.2 part per million in a test boiler operating at 200 pounds per square inch gauge pressure and a temperature of 390° F.

Industrial water treating systems which operate under sub-atmospheric pressures such as evaporators and vacuum distillation processes present special problems from the standpoint of foaming. Stability of the anti-foam composition is of particular importance in this use.

The compositions of the present invention can also be employed in sub-atmospheric pressure systems with good results. For this type of application, I prefer to employ the combination of the polyoxypropylene glycerol and a polyethylene glycol ester of an organic acid containing at least 12 carbon atoms per molecule. The molecular weight of the polyethylene glycol may range from about 200 to 2000 although a value of about 400 is preferred. When the polyethylene glycol esters are added in amounts from about 5 to 20% of the composition, a self-emulsifiable mixture results which has excellent stability characteristics.

The foam destroying tendencies of various compositions of the present invention, and the foam inhibiting properties of the compositions under sub-atmospheric pressure conditions are listed in the following tables:

Additive	Dosage, percent	Height of foam produced in mm. at specified time intervals (pressure of 100 mm. in boiler, heating element operating at 50 volts)				
		1 Min.	2 Min.	3 Min.	4 Min.	5 Min.
Blank		660	660	665	685	670
Polyglycol 11-200, 90%, Arquad 2C (75% Active), 10%	0.037	24	24	24	24	23
Polyglycol 11-300, 90%, Arquad 2C (75% Active), 10%	0.037	15	16	15	15	12
Polyglycol 11-400, 90%, Arquad 2C (75% Active), 10%	0.037	70	80	85	90	100

Additive	Dosage, percent	Foam height produced in mm. measured after boiling for specified intervals (pressure of 100 mm. in boiler, heating element operating at 100 volts)				
		10 Min.	15 Min.	20 Min.	25 Min.	30 Min.
Blank		1,255				
Polyglycol 11-200		165	170	130	140	165
Polyglycol 11-200 90%, Arquad 2C (75% Active), 10%	0.037	80	125	220	370	440
Polyglycol 11-300	0.037	150	105	100	75	75
Polyglycol 11-300 90%, Arquad 2C (75% Active), 10%	0.037	95	125	210	300	425
Polyglycol 11-400	0.037	87	92	90	95	98
Polyglycol 11-400 90%, Arquad 2C (75% Active), 10%	0.037	72	105	155	210	315
Polyglycol 11-400 90%, Polyethylene glycol 400 monooleate, 10%	0.037	80	90	85	97	110

Dosage levels employed will vary, of course, depending upon the severity of the foaming condition. However, as a general rule, it is advisable to add at least one part per million of the active ingredient up to about 500 parts per million both for purposes of foam destruction and foam inhibition. Larger amounts can be added, if desired, but generally are not required and are therefore not economical.

While the compositions of the present invention have particular utility in the prevention of foaming under conditions of boiling, they can also be employed to advantage in the treatment of other aqueous systems to inhibit, control, or destroy foam. One such application exists in the field of foaming ore flotation where the flotation water is recirculated rapidly in order to conserve water. Compositions of the present invention do not interfere with the production of the controlled foam necessary for ore flotation but are successful in destroying the foam after it leaves the flotation vats.

The compositions of the present invention also find use in other processes where foaming is a problem, particularly in the paper making industry for the treatment of paper producing stocks.

It will be evident that various modifications can be made to the described embodiment without departing from the scope of the present invention.

I claim as my invention:

1. A self-emulsifiable anti-foam composition consisting essentially of a mixture of polyoxypropylene glycerol having a molecular weight of at least 1000 and a quaternary ammonium salt having at least one hydrocarbon chain of at least 12 carbon atoms, said salt being present in an amount of from 5 to 20% by weight of said mixture.

2. A self-emulsifiable anti-foam composition consisting essentially of a mixture of a 1,2,3 polyoxypropylene glycerol having a molecular weight of from 1000 to 5000 and a quaternary ammonium salt having at least one hydrocarbon chain of at least 12 carbon atoms, said salt being present in an amount of from 5 to 20% by weight of said mixture.

3. The method of inhibiting foam formation in a system having a tendency to foam on boiling which comprises dispersing into said system a mixture of at least one part per million of a 1,2,3 polyoxypropylene glycerol having a molecular weight from 1000 to 5000 and a quaternary ammonium salt having at least one hydrocarbon chain of at least 12 carbon atoms, said salt being added in an amount of from 5 to 20% by weight of said mixture.

4. The method of inhibiting foam formation in a system having a tendency to foam which comprises dispersing into said system a mixture of at least one part per million of a polyoxypropylene addition product of trimethylolpropane, said addition product having a molecular weight of from 400 to 5000, and a quaternary ammonium salt having at least one hydrocarbon chain of at least 12 carbon atoms, said salt being present in an amount of from 5 to 20% by weight of said mixture.

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