

1

2,701,239

STEAM GENERATION AND COMPOSITIONS FOR INHIBITING FOAMING

John W. Ryznar, La Grange Park, Ill., assignor to National Aluminate Corporation, Chicago, Ill., a corporation of Delaware

No Drawing. Application January 16, 1952, Serial No. 266,777

15 Claims. (Cl. 252—321)

The present invention relates to improved antifoaming compositions which are added to water that is subjected to boiling, as in the boilers of locomotives, stationary steam generators, evaporators, and in other instances where the boiling of water occurs, especially under superatmospheric temperature and pressure conditions, whereby the tendency of the water therein to foam is prevented or reduced and the boiling characteristics of the water so improved that priming of the steam generator and carryover of boiler water with the steam therefrom is prevented.

It is well known that in the operation of steam boilers, such as in railroad locomotives, in electric power plants and the like, or in other boiling operations where steam is formed, as for example in evaporators, that the water therein, even though initially it shows little tendency to foam, will, when the amount of total dissolved solids approaches a relatively high concentration due to the production of steam, develop a very decided tendency to foam. This foaming of the water in a boiler producing steam is characterized not only by an accumulation of relatively stable froth or foam on the surface of the boiler water but also by the formation at the heat transfer surfaces in the boiler of extremely small steam bubbles. These minute bubbles show almost no tendency to coalesce and the result is that the entire volume of water in the steam generator is lifted in the form of so-called "light water," which is actually an intimate mixture of boiler water and tiny steam bubbles. When this occurs, considerable quantities of boiler water are physically carried out of the boilers or evaporators with the steam, thereby introducing solid matter into the steam lines and into the eventual condensate. Such carryover has many disadvantages because it tends to contaminate and restrict the steam lines, to plug or corrode the valves, to deposit on turbine blades, to plug and cause burning out of superheater tubes, and under serious conditions may even impair the cylinders and piston rods of steam engines or otherwise render the steam unfit for use. The carryover is frequently due in part, at least, to priming, or what may be described as surging or boiling over of the water.

Attempts have been made in the past to control foaming and priming by controlling the dissolved solids content of the water as by excessive blow-down of the boilers, that is, the removal, either continuously or periodically, of a portion of the boiler water containing the undesired excess solids. Also, it has been common to add materials for the purpose of abating the foam as by the injection of such materials as castor oil, tallow, and the like. While these fatty materials, notably castor oil, have some small degree of efficiency, they are, on the other hand, quite deficient in that they introduce new difficulties which, in some instances, are worse than the conditions they are intended to cure. In the first place, these fatty materials or glycerides are very unstable under severe hydrolytic conditions encountered in steam generation, particularly under the conditions of superatmospheric pressure, the corresponding high temperatures and the alkalinity of the boiler water. The resultant decomposition products which remain in the boiler tend to increase the foaming tendencies of the boiler water and to accumulate in such a way as to give a "compound dirty" boiler, necessitating frequent washing. Furthermore, in many instances cer-

2

tain of the decomposition products thus produced, or sometimes even the materials themselves, have a definite volatility with steam and will, therefore, steam-distill out of the steam generators, thus appearing in the steam and in the eventual condensate. This, of course, is also undesirable. Additionally, such types of antifoaming agents usually are of such a low order of efficiency that they have to be employed in relatively large quantities, adding not only to the expense but also to the inconvenience of operating the steam generators; and since they are so unstable their effectiveness is of short duration, necessitating the continual charging into the boilers or other steam generators of relatively large amounts of these older antifoaming agents.

The most noteworthy advance over the use of the fatty glycerides described above was the discovery and development of certain high molecular weight substituted polyamides, which antifoaming compounds overcame many of the disadvantages of the former, especially in that they were highly efficient at lower dosage levels and much more resistant to decomposition, so that their effective life was relatively greater.

One of the objects of this invention is to provide a new and improved process for preventing the foaming and priming of steam generators, thus improving the quality of the steam produced thereby.

Another object is to provide new and improved compositions for adding to the water in a steam generator to prevent or reduce its tendency to foam.

Another object is to provide antifoaming compositions which are effective to prevent foaming when used in very low dosages.

A further object is to provide highly effective antifoam compositions which are readily and easily dispersible when added to the feed water entering a steam generator.

Another object of this invention is to provide antifoam compositions in which the active effective ingredients are readily soluble in water at relatively low temperatures, (e. g., 75° F.) but decrease in solubility when the water is heated to relatively high temperatures such as are employed in the generation of steam under superatmospheric pressures and the corresponding temperatures.

Still another object of the invention is to provide a process of generating steam and new and improved antifoam compositions therefor wherein the period of effectiveness of the antifoam composition is greatly prolonged as compared to the period of effectiveness of other antifoam compositions presently known in the art.

Still another object of the invention is to provide a new and improved process of inhibiting foaming during steam generation which permits operations at higher dissolved solids contents than has heretofore been considered possible.

An additional object is to provide new and useful antifoaming compositions of an extremely high order of resistance to decomposition under the conditions prevailing in steam generation. Other objects will appear hereinafter.

The antifoam agents employed in accordance with this invention can be described as addition products of a primary and/or secondary amine and an alkylene oxide which is either ethylene oxide, 1,2-propylene oxide, or a mixture of ethylene oxide and 1,2-propylene oxide, the resultant addition product being substantially insoluble under steam generating conditions. The products employed for the purpose of the invention can also be described as amino ether alcohols characterized by a polyoxyalkylene group having different terminal groups connected to different carbon atoms, the oxyalkylene groups being either all oxyethylene, mixed oxyethylene and oxy-1,2-propylene groups, or all oxy-1,2-propylene groups. The preferred products have oxyalkylene groups derived from at least 1/3 part of 1,2-propylene oxide for each part of ethylene oxide by weight.

Where the initial reactants are an alkylene oxide and a monoamine, the resultant amino ether alcohols have different terminal groups connected to different carbon

atoms, one of said terminal groups being a hydroxy group and the other being a substituted amino group. If the amine initially employed contains a terminal primary amino group the terminal amino groups of the final product will be a secondary amino group. If the amine initially employed contains a terminal secondary amino group the terminal amino group of the final product will be a tertiary amino group.

Where the amine employed as one of the initial reactants is a polyamine the resultant compound contains amino groups linearly connected to polyoxyalkylene groups and the terminal groups are hydroxy groups. In other words, the amino groups are interiorly positioned in the structure of the compound and are not terminal groups.

The compounds which have proven to be satisfactory for the purpose of the invention have all been relatively high molecular weight compounds having a molecular weight of at least 1200.

Where monoamines are employed as the initial reactant useful compounds are obtained having molecular weights within the range of 1200 to 3000. Where polyamines are employed as the initial reactant, higher molecular weight compounds can be obtained. The molecular weight can be varied to some extent depending upon the molecular weight of the amine employed as the initial reactant but will usually be determined largely by the number of amino groups present in the amine and the quantity of the alkylene oxide that can be reacted therewith.

Increasing the proportion of 1,2-propylene oxide employed in the reaction tends to decrease the water solubility of the resultant compound. The compounds employed for the purpose of the invention are sometimes water soluble at ordinary temperatures (e. g. 75° F. to 100° F.) but must be substantially water insoluble at the steam generating temperature at which they are used. Good results are obtained where the amine employed as an initial reactant is water insoluble and the reaction product of the alkylene oxide and the amine are water soluble at ordinary temperatures and water insoluble under steam generating conditions. However, the initial reactant can be water soluble and the resultant end product can be water insoluble under ordinary and elevated temperature conditions.

It is preferable to employ for the purpose of the invention aliphatic amino ether alcohols characterized by a structure containing oxyethylene and oxy-1,2-propylene groups in the same molecule, having different terminal groups connected to different carbon atoms, one of said terminal groups being a hydroxy group and the other a substituted amino group, and having a molecular weight of at least 1200, the oxyethylene and the oxypropylene groups being derived from a weight ratio of 1,2-propylene oxide to ethylene oxide within the range of 1:3 to 9:1, preferably about 1:1.

Since, as indicated above, it is possible to prepare the ether alcohols of this invention by various routes, the invention should not be limited by the following examples, which are merely intended to illustrate some satisfactory procedures for preparing a few of the materials suitable for employment within the scope of the present invention.

EXAMPLE I

A mixture of equal parts of ethylene oxide and 1,2-propylene oxide was supplied to a reactor charged with 20 parts of n-butylamine and 0.8 part of dry powdered sodium hydroxide. The ethylene oxide had a water content of about 0.09% and an acetaldehyde content of about 0.06% and the 1,2-propylene oxide had a water content of about 0.05% and a propionaldehyde content of about 0.15%. The n-butylamine was substantially anhydrous. The pressure maintained during the introduction of the oxide mixture was about 5 to 22 p. s. i. (pounds per square inch gauge) over a period of about 2 hours and, thereafter, the mixture was cycled for a period of an additional hour. During the reaction the temperature was held at 90 to 100° C.

Following the same procedure additional amine diol compositions having an oxide ratio of 1:1 were produced by utilizing the product of one reaction as a starting material for compositions of higher viscosity and increased average molecular weight.

The following products possess properties and specifications as presented in the following table:

Example.....	A	B	C	D
Viscosity:				
SUS at 100° F.....	607	1, 613	1, 776	2, 098
SUS at 210° F.....	103	259	289	335
Average Molecular Weight, Menzies-Wright.....	1, 269	2, 388	2, 325	2, 396
Specific Gravity, 20/20° C.....	1. 0530	1. 0573	1. 0598	1. 0645
Flash Point, ° F.....	468	460	440	485
Fire Point, ° F.....	564	585	515	560
Water, Percent.....	0. 84	0. 39	0. 37	0. 61
pH of 5% Aqueous Solution.....	10. 7	9. 98	10. 0	8. 96

EXAMPLE II

A mixture containing equal parts of ethylene oxide and 1,2-propylene oxide was supplied to a reactor charged with 20 parts of di-n-butylamine and 0.8 part of dry powdered sodium hydroxide. The pressure maintained during the introduction of the oxide mixture was about 10 to 30 p. s. i. over a period of about 2 hours and, thereafter, the mixture was cycled for a period of about 1 hour. During the reaction the temperature was held at 90 to 115° C.

Following the same procedure additional amine oxyalkylol compositions having an ethylene oxide to 1,2-propylene oxide ratio of 1:1 were produced utilizing the product of one reaction as a starting material for compositions of higher viscosity and increased average molecular weight.

The following products possessed properties and specifications as presented in the following table.

Example.....	A	B	C
Viscosity:			
SUS at 100° F.....	588	1, 373	2, 855
SUS at 210° F.....	107	225	456
Average Molecular Weight, Menzies-Wright.....	1, 220	2, 170	2, 860
Specific Gravity, 20/20° C.....	1. 0411	1. 0538	1. 0568
Flash Point, ° F.....	386	415	437
Fire Point, ° F.....	495	515	510
Water, Percent.....	0. 25	0. 80	0. 58
pH of 5% aqueous solution.....	11. 0	10. 8	10. 6

The products employed as herein described may be liquids or low-melting wax-like solids, and may be entirely soluble in cold water or only partially soluble. In the latter case, they are relatively easily dispersed in the feedwater by means of additional dispersing agents, as described below. All of the products exhibit substantial insolubility in hot water, the phenomenon of decreasing solubility in water with increasing temperature being characteristic of compounds of this class which contain multiple ether linkages and in which the ratio of ether linkages to carbon is sufficiently great to permit the weak hydrogen bonding effect of the ether oxygen to confer water solubility.

The amounts of an antifoam agent employed in inhibiting the foaming of water in a steam generator will depend upon several factors, among them the per cent of solids in the foaming liquid, the nature of the solids, the alkalinity, temperature, and pressure, the type and degree of circulation in the steam generator, the rate of steam production, and the amount of foam suppression desired. It is, therefore, impossible to state any rigid rules for estimating the amount of an antifoam which needs to be used. The amounts of the amino ether alcohols of this invention which are required are, however, extremely small. For many purposes, amounts of the order of 0.01 grain per gallon to 0.02 grain per gallon in the feedwater are sufficient, and under certain conditions quantities as low as 0.001 grain per gallon in the feedwater have proved effective. In general, it can be said that quantities greater than 0.1 grain per gallon in the feedwater would seldom be required.

The previously described proportions can be converted from grains per gallon to parts per million by multiplying the grains per gallon by the factor 17.1.

By way of illustrating the remarkable effectiveness of the amino ether alcohols of this invention, the method of testing their antifoam efficiency will be described and exemplary data given.

In the laboratory, the experimental boiler used was of the type described in the publication "Solid Matter in

5

Boiler Water Foaming," by Foulk and Brill, which appeared in the periodical Industrial and Engineering Chemistry, volume 27, pages 1430-35. This boiler was fitted with sight glasses on each side of the steam release space so that conditions in the boiler in a zone several inches above and below the normal water level were observed while the boiler was operating under pressure. It was also equipped with an automatic water level control which held the water level within a range of ± 0.25 inch.

In the series of tests described below, a feedwater (herein referred to as a 210 grain water) was used having the following composition, expressed in parts per million, by weight, with an M alkalinity of 30% of the dissolved solids.

Calcium hardness-----	(as CaCO_3)--	178.0
Magnesium hardness-----	(as CaCO_3)--	185.0
Alkalinity (methyl orange)-----	(as CaCO_3)--	1370.0
Sodium chloride-----	(as NaCl)--	334.0
Sodium sulfate-----	(as Na_2SO_4)--	1950.0
Tannin extract, dry-----		51.0

To this feedwater was added the antifoam composition of the character and in the quantity specified in the specific experiment, and this water was then gradually concentrated in the test boiler by evaporation at the rate of six gallons per hour at 250 pounds per square inch (p. s. i.) gauge pressure. A continual recording was made of the relative conductivity of the condensate from the boiler, and continual observations were made of the character of the boiling and the amount of foaming as seen through the sight glasses. When the antifoam thus introduced continuously with the feedwater was no longer able to overcome the foaming tendencies brought about by the concentration of dissolved solids in the boiler water, the foam height became great enough to cause boiler water to be carried out of the boiler with the steam, and this end-point of the test was determined both by observation through the sight glasses and, particularly, by the abrupt increase in the conductivity of the steam, as shown in the continuous recorder. At this end-point, a sample of the boiler water was withdrawn from the boiler and analyzed, and the effectiveness of the antifoam expressed in terms of the total dissolved solids concentration which it permitted the boiler to carry. A high value of total dissolved solids (TDS) indicates an effective antifoam. With no antifoam, this feedwater gives a carryover at a total dissolved solids value of approximately 252 grains per gallon.

The compositions described as Ucon materials were made by Carbide and Carbon Chemicals Corporation. In these compositions the letter "H" signifies that the compositions are heteric in that they are made from both ethylene oxide and 1,2-propylene oxide. The letters "BA" indicate that the amine employed as an initial reactant is butyl amine. The letters "DBA" indicate that the amine employed as an initial reactant is dibutylamine.

EXAMPLE III

The material tested as an antifoam in this test was "UCON 50 HBA 607" which is the monobutyl amine derivative of a polyoxyalkylene glycol containing a weight ratio of ethylene oxide to propylene oxide of 1:1, and possessing an average total molecular weight of approximately 1269 as determined by calculation from data obtained by the Menzies-Wright method and a viscosity at 100° F. of 607 S. U. S. This material was completely soluble in the feedwater at room temperature, and was dissolved in the feedwater at a dosage of 0.005 grain per gallon. Carryover did not occur until the total dissolved solids in the boiler water had reached 596 grains per gallon.

EXAMPLE IV

Under the same test conditions the composition identified as UCON 50-HBA-1613, which is the addition product with butylamine of ethylene oxide and 1,2-propylene oxide in a weight ratio of approximately 1:1 having a molecular weight of approximately 2400, was tested and carryover did not occur until the total dissolved solids in the boiler water had reached 4427 grains per gallon.

EXAMPLE V

Under the same test conditions the composition identified as UCON 50-HBA-1776, which is the addition product with butylamine of ethylene oxide and 1,2-propylene oxide in a weight ratio of approximately 1:1 having a

6

molecular weight of approximately 2300, was tested and carryover did not occur until the total dissolved solids in the boiler water had reached 4417 grains per gallon.

EXAMPLE VI

Under the same test conditions the composition identified as UCON 50-HBA-2098, which is the addition product with butylamine of ethylene oxide and 1,2-propylene oxide in a weight ratio of approximately 1:1 having a molecular weight of approximately 2400, was tested and carryover did not occur until the total dissolved solids in the boiler water had reached 5764 grains per gallon.

EXAMPLE VII

Under the same test conditions the composition identified as UCON 50-HDBA-588, which is the addition product with dibutylamine of ethylene oxide and 1,2-propylene oxide in a weight ratio of approximately 1:1 having a molecular weight of approximately 1200, was tested and carryover did not occur until the total dissolved solids in the boiler water had reached 391 grains per gallon.

EXAMPLE VIII

Under the same test conditions the composition identified as UCON 50-HDBA-1373, which is the addition product with dibutylamine of ethylene oxide and 1,2-propylene oxide in a weight ratio of approximately 1:1 having a molecular weight of approximately 2200, was tested and carryover did not occur until the total dissolved solids in the boiler water had reached 4576 grains per gallon.

EXAMPLE IX

Under the same test conditions the composition identified as UCON 50-HDBA-2855, which is the addition product with dibutylamine of ethylene oxide and 1,2-propylene oxide in a weight ratio of approximately 1:1 having a molecular weight of approximately 2900, was tested and carryover did not occur until the total dissolved solids in the boiler water had reached 3416 grains per gallon.

The above examples cover the employment of compositions derived from monobutylamine and dibutylamine. Similarly, any other primary or secondary amine can be used as one of the initial reactants to yield products having valuable antifoam characteristics. This reaction is only limited to those amine compositions having 1 or 2 replaceable hydrogen atoms attached directly to the nitrogen atom. Hence, primary and secondary amines of the alkyl series, the cycloalkyl series, aryl series and aralkyl series are suitable. Typical specific examples of suitable monoamines are amylamine and diamylamine, cyclohexylamine and dicyclohexylamine, aniline and diphenyl amine, benzyl amine and dibenzyl amine, methyl amine and dimethyl amine, ethyl amine and diethyl amine, isopropyl amine and diisopropyl amine, butyl amine and dibutyl amine, decylamine and didecylamine, dodecylamine and didodecylamine, octadecylamine and dioctadecylamine, alpha-naphthylamine and beta-naphthylamine. Typical specific examples of suitable polyamines are ethylene diamine, propylene diamine, butylene diamine, decamethylene diamine, diethylene triamine, triethylenetetramine, tetraethylenepentamine, diisopropylenetriamine, triisopropylenetetramine, o-, m- and p-phenylene diamine, benzidine and naphthylenediamines. The preferred compositions are those in which the amine reactant is initially water insoluble. The preferred compositions also are those in which the composition as a whole is aliphatic rather than aromatic.

One of the difficulties of using most antifoam materials is that of conveniently introducing them into the water in small, controlled amounts so that their maximum effectiveness is utilized. While many of the amino ether alcohols employed in accordance with this invention are readily soluble in cold water, others are not completely soluble and must be rendered readily dispersible for use. Liquids, waxes, and preformed emulsions are inconvenient to apply to the feedwaters used by locomotives and other power plants. It is thus a further object of this invention to provide the amino ether alcohols compounded with other water treating chemicals in a powdered or briquetted form which can readily and conveniently be added to water, and which will disperse in the water quickly without excessive agitation or mixing.

The amino ether alcohols employed in the practice of this invention can all be incorporated into dry powdered

materials such as powdered tannin, sodium lignin sulfonate, desulfonated lignin, soda ash, various orthophosphates and polyphosphates. Depending somewhat upon the powdered absorbent selected, amounts of the amino ether alcohols of the order of 5 to 10% of the total composition may be readily incorporated to give a dry-appearing pulverized product. By the use of suitable binders and other well known techniques, such compositions may also be briquetted.

The resulting dry-appearing products just described are readily and completely dispersible in water when the amino ether alcohols themselves are soluble or dispersible. When aminoether alcohols are employed which are substantially insoluble in water, these, too, give dry-appearing compositions by the method described if a dispersing agent is used in conjunction with them. In fact, many of the common water treating chemicals of a tannin or lignin nature behave as sufficiently powerful dispersants to readily disperse the insoluble amino ether alcohols in the form of a relatively stable aqueous dispersion. Where it is not desired to use the tannins or lignin derivatives in quantity sufficient to act as dispersants for the amino ether alcohols, a small amount of soap, such as the alkali metal soaps of oleic acid or tall oil, or a sulfonated oil, may be employed with good results, and the amount of soap or sulfonate thus required is insufficient to interfere with the powerful antifoam effect of the ether alcohols or to render the boiler "compound dirty."

In general, then, the amino ether alcohols of this invention may be prepared in the form of dry-appearing pulverized or briquetted compositions which are readily and completely dispersible in water with a minimum of agitation by incorporating them, with or without a dispersant such as soap or sulfonated oil, with various tannins, lignins, or other pulverized chemicals, either alone or in combination.

A few examples will serve to illustrate the preparation of suitable dry-appearing, dispersible compositions.

EXAMPLE A

	Per cent
Amino ether alcohols described in Examples I to IX	3
Desulfonated lignin	97

The liquid amino ether alcohol was incorporated with the dry, pulverized lignin derivative by adding the amino alcohol to the latter in a putty-chaser type mixer. The resultant composition was dry and free flowing and was readily dispersible in water in concentrations of 3 to 5% or greater.

EXAMPLE B

	Per cent
Amino ether alcohols described in Examples I to IX	8
Soda ash	72
Sodium septaphosphate	20

The mixing was done as described in Example A by adding the liquid to the mixed dry solids. The resultant pulverized product was readily and completely soluble in cold water.

EXAMPLE C

	Per cent
Amino ether alcohols of Examples I to IX	3
Desulfonated lignin	97

This composition was mixed as in Example A and the dry composition obtained was readily and completely dispersible in water in a concentration of 3 to 5%.

EXAMPLE D

	Per cent
Amino ether alcohols of Examples I to IX	3
Refined tall oil	2
Desulfonated lignin derivative	95

This composition was readily and completely dispersible in water, the residual alkalinity of the lignin derivative serving to convert the refined tall oil to soap when the composition was added to water.

EXAMPLE E

	Per cent
Amino ether alcohols of Examples I to IX	3
Sodium lignin sulfonate	97

The lignin derivative used herein was that obtained directly from the sulfite pulp manufacturing process after removal of the bulk of the wood sugars, converting the calcium sulfonate to the corresponding sodium salts, and drying.

The composition described was readily dispersible in water.

In general where the amino ether alcohol is incorporated with tannins, sodium lignin sulfonate and desulfonated lignins prior to adding it to the boiler feedwater, the quantity of the amino ether alcohol is within the range of 0.5% to 12% by weight of the total composition and the total quantity of tannins, sodium lignin sulfonate and/or desulfonated lignins is within the range of about 50% to about 88% by weight of the composition.

The practice of the invention is applicable to the inhibition of foaming in steam generation over a relatively wide pressure and temperature range. In locomotive boilers, steam is generally generated at pressures around 250 pounds per square inch and the corresponding temperatures. Excellent results have been obtained with the practice of the invention at pressures within the range of 100 to 300 pounds per square inch and the corresponding temperatures. The invention can also be used, however, in connection with the generation of steam at much higher pressures and the corresponding temperatures, as, for example, in stationary boilers operating at pressures as high as 1000 to 1500 pounds per square inch. The compositions employed in accordance with the invention are effective not only in inhibiting foaming but also in conditioning and improving the quality of the steam. For this purpose, they may be used in even smaller amounts than the amounts required for the complete inhibition of foaming and priming.

The amino ether alcohols employed in the practice of this invention are desirably used in conjunction with other organic water treating chemicals of the tannin and lignin types in treating many water supplies as will be seen from the following. On waters high in magnesium salts in which the magnesium in the boiler will generally be in the form of magnesium hydroxide, it is desirable that sufficient of hydroxylated organic material such as tannins, tannic acid, gallic acid, pyrogallol, catechol, phloroglucinol, etc., be added along with the amino ether alcohols. These hydroxylated organic compounds have the ability of nullifying the bad effects of the magnesium hydroxide. Magnesium hydroxide appears to partially selectively adsorb the antifoam material and so take it out of the boiler water so that the full antifoam action cannot be exerted by the antifoam compositions when in this adsorbed state. However, when an organic material such as a tannin is added, magnesium hydroxide appears to lose its ability to interfere with the antifoam action. Inasmuch as most boiler feedwaters encountered will have varying amounts of magnesium salts present, it is desirable that such hydroxylated organic compounds be mixed with the polyether alcohols prior to addition to the boiler feedwater.

It will be understood that the tannins, sodium lignin sulfonate and/or desulfonated lignins are not necessarily incorporated with the antifoam composition prior to the addition of the latter to the feedwater. Where it is desirable to use tannins, sodium lignin sulfonate and/or desulfonated lignins, these substances may also be added directly to the boiler water. The following table illustrates the quantity of the tannins, sodium lignin sulfonate and/or desulfonated lignins which can be employed satisfactorily to nullify the action of the magnesium salts on the amino ether alcohol antifoam ingredients.

Table I

Magnesium— Grains per Gallon in Boiler Water (expressed as CaCO ₃)	Tannins, Sodium Lignin Sulfonate and/or Desulfonated Lignins Grains per Gallon in Boiler Water
0	0
1-5	0.5-1
5-10	1-2
10-20	2-3

Thus another advantage is evident in preparing and using the pulverized or briquetted compositions hereinabove described containing both the amino ether alcohol antifoam and the polyhydroxylated organic material of the tannin or lignin-derivative type.

As will be apparent from the foregoing description, the compounds employed in accordance with the invention do not all give the same results and from that standpoint

are not necessarily equivalents. Some of these amino ether alcohol compositions, especially those of the type referred to in Examples IV, V, VI, VIII and IX, are exceptional in their foam inhibiting properties.

The invention is hereby claimed as follows:

1. A method of generating steam from a boiler water having a tendency to foam on boiling which comprises dispersing in said water a quantity of an addition product of an amine from the group consisting of primary and secondary amines and an alkylene oxide from the group consisting of ethylene oxide, 1,2-propylene oxide and mixtures of both ethylene oxide and 1,2-propylene oxide, the average molecular weight of said addition product being at least 1200 and said addition product being substantially insoluble in said boiler water at the temperature of steam generation, the quantity of said addition product being effective to inhibit the tendency of said water to foam on boiling, and heating the resultant aqueous dispersion to the boiling point.

2. A method of generating steam from a boiler water having a tendency to foam on boiling and which contains magnesium compounds which comprises dispersing in said water a quantity of an addition product of an amine from the group consisting of primary and secondary amines and an alkylene oxide from the group consisting of ethylene oxide, 1,2-propylene oxide and mixtures of both ethylene oxide and 1,2-propylene oxide, the average molecular weight of said addition product being at least 1200 and said addition product being substantially insoluble in said boiler water at the temperature of steam generation, and a quantity of a hydroxylated organic compound from the group consisting of tannins, sodium lignin sulfonate and desulfonated lignins effective to nullify the action of said magnesium compounds on said addition product, the quantity of said addition product being effective to inhibit the tendency of said water to foam on boiling, and heating the resultant aqueous dispersion to the boiling point.

3. A method of generating steam from a boiler water having a tendency to foam on boiling which comprises dispersing in said water a quantity of an amino ether alcohol characterized by a polyoxyalkylene chain having different terminal groups connected to different carbon atoms, one of said terminal groups being a hydroxy group and the other being an amino group, said amino ether alcohol having a molecular weight of at least 1200, the oxyalkylene groups in said amino ether alcohol being from the group consisting of oxyethylene and oxy-1,2-propylene groups and being derived from at least $\frac{1}{3}$ part of 1,2-propylene oxide for each part of ethylene oxide by weight, said amino ether alcohol being substantially insoluble in said boiler water at the temperature of steam generation and the quantity of said amino ether alcohol being effective to inhibit the tendency of said water to foam on boiling, and heating the resultant aqueous dispersion to the boiling point.

4. A method of generating steam from a boiler water having a tendency to foam on boiling and which contains magnesium compounds which comprises dispersing in said water a quantity of an amino ether alcohol characterized by a polyoxyalkylene chain having different terminal groups connected to different carbon atoms, one of said terminal groups being a hydroxy group and the other being an amino group, said amino ether alcohol having a molecular weight of at least 1200, the oxyalkylene groups in said amino ether alcohol being from the group consisting of oxyethylene and oxy-1,2-propylene groups and being derived from at least $\frac{1}{3}$ part of 1,2-propylene oxide for each part of ethylene oxide by weight, said amino ether alcohol being substantially insoluble in said boiler water at the temperature of steam generation, and a quantity of a hydroxylated organic compound from the group consisting of tannins, sodium lignin sulfonate and desulfonated lignins effective to nullify the action of said magnesium compounds on said addition product, the quantity of said amino ether alcohol addition product being effective to inhibit the tendency of said water to foam on boiling, and heating the resultant aqueous dispersion to the boiling point.

5. A method of generating steam from a boiler water having a tendency to foam on boiling which comprises dispersing in said water a quantity of an addition product of an aliphatic monoamine from the group consisting of primary and secondary aliphatic monoamines and an alkylene oxide from the group consisting of 1,2-propylene oxide and mixtures of both ethylene oxide and 1,2-propyl-

ene oxide containing at least $\frac{1}{3}$ part by weight of 1,2-propylene oxide per part of ethylene oxide, the average molecular weight of said addition product being at least 1200 and said addition product being substantially insoluble in said boiler water at the temperature of steam generation, the quantity of said addition product being effective to inhibit the tendency of said water to foam on boiling, and heating the resultant aqueous dispersion to the boiling point.

6. A method of generating steam from a boiler water having a tendency to foam on boiling and which contains magnesium compounds which comprises dispersing in said water a quantity of an addition product of an aliphatic monoamine from the group consisting of primary and secondary aliphatic monoamines and an alkylene oxide from the group consisting of 1,2-propylene oxide and mixtures of both ethylene oxide and 1,2-propylene oxide containing at least $\frac{1}{3}$ part by weight of 1,2-propylene oxide per part of ethylene oxide, the average molecular weight of said addition product being at least 1200 and said addition product being substantially insoluble in said boiler water at the temperature of steam generation, and a quantity of a hydroxylated organic compound from the group consisting of tannins, sodium lignin sulfonate and desulfonated lignins effective to nullify the action of said magnesium compounds on said addition product, the quantity of said addition product being effective to inhibit the tendency of said water to foam on boiling, and heating the resultant aqueous dispersion to the boiling point.

7. A process of minimizing the production of foam in and the priming of steam generators operating under superatmospheric pressure conditions which comprises incorporating with a water therein containing an amount of total dissolved solids tending to produce foaming and priming a quantity of a foam inhibiting composition within the range of 0.001 grain to 0.1 grain of said compound per gallon of said water, said composition being an addition product of an amine from the group consisting of primary and secondary amines and a mixture of both ethylene oxide and 1,2-propylene oxide containing at least $\frac{1}{3}$ part by weight of 1,2-propylene oxide per part of ethylene oxide, the addition product being water insoluble under steam generating conditions and the molecular weight of the addition product averaging at least 1200.

8. The process of minimizing the production of foam in steam boilers during steam generation which comprises incorporating in a water therein containing an amount of total solids tending to produce foaming a quantity of an addition product of butylamine and mixtures of both ethylene oxide and 1,2-propylene oxide containing at least $\frac{1}{3}$ part of 1,2-propylene oxide per part of ethylene oxide, the average molecular weight of said addition product being at least 1200 and said quantity being sufficient to substantially inhibit said foaming.

9. The process of minimizing the production of foam in steam boilers during steam generation which comprises incorporating in a water therein containing an amount of total solids tending to produce foaming an addition product of dibutylamine and a mixture of both ethylene oxide and 1,2-propylene oxide containing at least $\frac{1}{3}$ part of 1,2-propylene oxide per part of ethylene oxide, the average molecular weight of said addition product being at least 1200 and said quantity being sufficient to substantially inhibit said foaming.

10. The process of minimizing the production of foam in steam boilers during steam generation which comprises incorporating in a water therein containing an amount of total solids tending to produce foaming an addition product of butylamine and a mixture of both ethylene oxide and 1,2-propylene oxide in approximate weight ratio of 1:1, the average molecular weight of said addition product being at least 1200 and said quantity being sufficient to substantially inhibit said foaming.

11. The process of minimizing the production of foam in steam boilers during steam generation which comprises incorporating in a water therein containing an amount of total solids tending to produce foaming an addition product of dibutylamine and a mixture of both ethylene oxide and 1,2-propylene oxide in approximate weight ratio of 1:1, the average molecular weight of said addition product being at least 1200 and said quantity being sufficient to substantially inhibit said foaming.

12. A liquid for the generation of steam comprising

11

a water containing an amount of total dissolved solids tending to produce foaming and priming when heated to the boiling point and 0.001 grain to 0.1 grain per gallon of said water of an addition product of an amine from the group consisting of primary and secondary amines and an alkylene oxide from the group consisting of ethylene oxide, 1,2-propylene oxide and mixtures of both ethylene oxide and 1,2-propylene oxide, the average molecular weight of said addition product being at least 1200 and said addition product being substantially insoluble in said boiler water at the temperature of steam generation.

13. A liquid for the generation of steam comprising a water containing magnesium compounds and an amount of total dissolved solids tending to produce foaming and priming when heated to the boiling point and 0.001 grain to 0.1 grain per gallon of said water of an amino ether alcohol which is an addition product of an amine from the group consisting of primary and secondary amines and an alkylene oxide from the group consisting of ethylene oxide, 1,2-propylene oxide and mixtures of both ethylene oxide and 1,2-propylene oxide, the average molecular weight of said addition product being at least 1200 and said addition product being substantially insoluble in said boiler water at the temperature of steam generation, and a quantity of a hydroxylated organic compound dispersed in said water from the group consisting of tannins, sodium lignin sulfonate and desulfonated lignins, said quantity being effective to nullify the action of the magnesium compounds on said addition product.

14. An antifoam composition for minimizing the production of foam in the generation of steam from water

12

which comprises essentially 0.5 to 12% by weight of an addition product of an amine from the group consisting of primary and secondary amines and an alkylene oxide from the group consisting of ethylene oxide, 1,2-propylene oxide and mixtures of both ethylene oxide and 1,2-propylene oxide, the average molecular weight of said addition product being at least 1200 and said addition product being substantially insoluble in boiler water at steam generating temperatures, and 50% to 88% by weight of a substance from the group consisting of tannins, sodium lignin sulfonate and desulfonated lignins.

15. A method of generating steam from a boiler water having a tendency to foam on boiling which comprises dispersing in said water a quantity of an addition product of an amine from the group consisting of primary and secondary amines and an alkylene oxide from the group consisting of ethylene oxide, 1,2-propylene oxide and mixtures of both ethylene oxide and 1,2-propylene oxide, the average molecular weight of said addition product being within the range from 1200 to 3000 and said addition product being substantially insoluble in said boiler water at the temperature of steam generation, the quantity of said addition product being effective to inhibit the tendency of said water to foam on boiling, and heating the resultant aqueous dispersion to the boiling point.

References Cited in the file of this patent

UNITED STATES PATENTS

2,233,383	De Groote et al. -----	Feb. 25, 1941
2,575,276	Jacoby et al. -----	Nov. 13, 1951