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STEAM GENERATION AND COMPOSITIONS FOR INHIBITING FOAM THEREIN

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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 transfor 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 certain 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.

In accordance with this invention, it has now been discovered that there is a series of compounds that are very effective when used as antifoaming and antipriming agents in steam generators and which may be broadly designated as high molecular weight polyoxyalkylene diols, characterized by the presence in the polyoxy-

alkylene chain of one or more oxymethylene groups. These diols possess several important advantages over formerly known antifoam compositions. They are all much more effective than any of the fatty glycerides, and many are more effective than any hitherto known materials. Furthermore, they are much more stable to decomposition under conditions of use than any of the glycerides or polyamides, thus giving them a greatly prolonged period of effectiveness in preventing foaming. In general, they are more readily dispersed in the water being fed to the steam generator than are older materials, and a further advantage offered by many of these diols is that they are liquids or very low-melting waxy materials which are readily soluble at ordinary temperatures.

The diols preferably employed in the practice of this invention may be represented by the structural formula

$$HO[(C_nH_{2n}O)_xCH_2O]_y(C_nH_{2n}O)_xH$$

wherein n is an integer equal to 2 or more, and may have several values in the same compound, and x and y are integers of one or more. Such compounds are thus seen to include polyoxyalkylene diols, in the polyoxyalkylene chain of which appears at least one oxymethylene group, and in which there are also other (larger) oxyalkylene groups. By these "larger" oxyalkylene groups is meant oxyalkylene groups which are not oxymethylene or substituted oxymethylene groups. Examples of these large oxyalkylene groups are

Oxyethylene

$$(-OCH_2CH_2-)$$

Oxypropylene

$$(-OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}- \text{ and } -OCH_2CH_2CH_2-)$$

Oxybutylene

$$(-OC_2H_4\underset{\displaystyle CH_3}{\underset{|}{CH}}-,\ -OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2-,\ -OCH_2CH_2CH_2CH-$$

$$-OCH\underset{\displaystyle CH_3}{\underset{|}{-}}CH-\underset{\displaystyle CH_3}{\underset{|}{}}$$

and

$$-OCH_2\underset{\displaystyle C_2H_5}{\underset{|}{CH}})$$

and oxyalkylenes of greater number of carbons such as oxypentamethylene, oxyhexamethylene, oxydecamethylene and higher homologues. The larger oxyalkylene groups present in the polyoxyalkylene chain may all be the same, or they may be different, so that several are present in the same chain. When the larger oxyalkylene groups are not all the same, they may occur in the chain in various proportions and in a random or irregular sequence, with respect to each other.

In order that these diols possess the property of efficiently preventing the foaming and priming of steam generators, they should be of relatively high molecular weight, i. e., either x or y, or both, in the formula should be of such size that the total molecular weight of the diol will be greater than a certain value. Since, as will be seen by the discussion to follow hereinafter, the usual synthetic methods for the production of the diols of this invention leads to a mixture of products very closely similar in chemical structure but of differing molecular size, it is only possible, in speaking of the molecular weight of these compounds, to refer to an average value of molecular weight for the mixture of polymers.

The products employed in accordance with the invention may also be described as addition products of formaldehyde with aliphatic dihydric alcohols. It is essential for the purpose of the invention that the addition products be substantially insoluble in the boiler water under the conditions of steam generation. Many of these

addition products have the advantage that they are substantially soluble in water at room temperatures of say 75° F. or even at somewhat higher temperatures used in preheaters, and hence can be readily dispersed in the boiler feedwater. They are further characterized, however, by the fact that they decrease in solubility upon heating to steam generating temperatures. The molecular weight of the addition product and the kind and type of oxyalkylene groups therein are all factors contributing to its water insolubility at the elevated temperatures used in steam generation. In view of the characteristic of decreasing solubility of these addition products with increasing temperatures, the temperature at which the steam is generated is also a factor. Thus, compounds which do not have the desired antifoam efficiency in boilers operating at 250 pounds per square inch may have such efficiency in boilers operating at 1000 to 1500 pounds per square inch. Routine tests can be used to determine whether a given addition product has the requisite insolubility under the steam generating conditions to be used.

It will be noted in the foregoing formula that n must have a value of at least 2. In other words, the aliphatic dihydric alcohol from wihch the addition products are prepared must have their hydroxy groups spaced by at least four carbon atoms. Vicinal glycols, which have hydroxy groups too close to each other, tend to form ring compounds such as dioxolane or dioxolane derivatives and are unsuitable for the purpose of the invention.

The oxymethylene group in the addition product is supplied by the formaldehyde reactant.

The addition products are prepared with formaldehyde because it forms compounds of high molecular weight when reacted with low molecular weight aliphatic dihydric alcohols. Other aldehydes and ketones do not react so readily and usually form only a dimer of the aliphatic dihydric alcohol. The preferred reactants used to form the addition products are formaldehyde and polyoxyalkylene glycols containing two to five carbon atoms in their oxyalkylene groups. The oxyethylene group is relatively hydrophilic and hence where the polyoxyalkylene glycol reacted with the formaldehyde contains all oxyethylene groups relatively high molecular weights must be attained in order to secure the desired insolubility in the hot boiler water. Higher oxyalkylene groups such as those derived from 1,2-propylene oxide are more hydrophobic and where these groups are present as the sole oxyalkylene groups in the polyoxyalkylene glycol, the addition product can have a much lower molecular weight.

The reaction between the formaldehyde and the aliphatic dihydric alcohol is carried out in the presence of a suitable catalyst either under dehydrating conditions or, alternatively, the aliphatic dihydric alcohol can first be reacted with the formaldehyde and then the water formed in the reaction can be removed from the reaction zone.

The reaction between the glycol and the formaldehyde is preferably carried out at moderate temperatures, for example, between 50° C. and 135° C., with or without a solvent as a diluent. To accelerate the reaction Friedel-Crafts catalysts are preferably employed, for example, aluminum chloride, ferric chloride, titanium tetrachloride, stannic chloride, borontrifluoride, and acid compounds such as sulfuric acid, benzene sulfonic acid or acid cation exchangers containing strongly acidic groups such as the sulfonated polymer of styrene and divinylbenzene, sulfonated phenolformaldehyde resin, sulfonated coal or the like.

The reaction is preferably carried out under very strong dehydrating conditions facilitating the removal of water from the reaction mixture. In the practice of the invention two different methods have been employed effectively. In one case aromatic hydrocarbons, such as benzene, toluene or xylene, which form azeotropes with water were distilled from the reaction zone. The water formed in

the reaction was thus continuously eliminated and very strong dehydrating conditions existed. In the second method the water was removed under vacuum using a slow stream of dry air to give the strong dehydrating conditions necessary. Other methods of preparation in which very strong dehydration conditions exist are also suitable for the preparation of the compounds of this invention.

In order to separate and collect the water formed in the reaction it is convenient to carry out the reaction in benzene solution. The benzene is distilled slowly and the water distilling with the benzene is separated. The benzene is then returned to the reaction zone. The water collected is measured and the progress of the reaction can be followed in this way. A convenient apparatus for carrying out this reaction consists of a Dean-Stark moisture trap fitted with a reflux condenser and a round bottom boiling flask. A tube full of a desiccant, such as calcium chloride, is preferably attached to the open end of the reflux condenser to prevent the condensation of the moisture from the atmosphere.

The formaldehyde used in the reaction can be added as an aqueous solution called formalin, or as solid trioxane (alpha-trioxymethylene). The solid alpha-trioxymethylene is preferred since the amount of water formed in the reaction is preferably used as a guide in following the extent of the reaction. It is well known that trioxane (alpha-trioxymethylene) decomposes to liberate monomeric formaldehyde when heated in the presence of acidic materials such as zinc chloride, ferric chloride, etc.

The products employed for the purpose of the invention have relatively high molecular weights, preferably at least 1000 and in some cases as high as 11,500, or higher.

In order to evaluate the effectiveness of these addition products tests were made on an experimental boiler of the type described in the publication "Solid matter in boiler water foaming" by Foulk and Brill, which appeared in the periodical Industrial and Engineering Chemistry, vol. 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 experiments described below, a feedwater (herein referred to as a 70 grain water) was used having the following composition, expressed in parts per million, by weight:

Calcium hardness (as $CaCO_3$)	154.0
Magnesium hardness (as $CaCO_3$)	154.0
Alkalinity (methyl orange) (as $CaCO_3$)	726.0
Sodium chloride (as NaCl)	85.5
Sodium sulfate (as Na_2SO_4)	718.0
Tannin extract, dry	34.2

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 (T. D. S.) indicates an effective antifoam. With no antifoam, this feedwater gives a carryover at a total dissolved solids value of approximately 175 grains per gallon.

The following examples illustrate some of the results of these tests.

EXAMPLE I

The material tested was an addition product of alpha trioxymethylene with Carbowax 1000 and Polyglycol P–400 in approximate molar ratios of 2:1:1 and having an intrinsic viscosity in benzene of 0.0915. At a dosage of 0.005 grain per gallon of feedwater the total dissolved solids in the boiler water averaged 733 grains per gallon in two tests before carryover occurred.

EXAMPLE II

The material tested was an addition product of alpha trioxymethylene with Carbowax 1000 and Polyglycol P–400 in approximate molar ratios of 2:1:1 and having an intrinsic viscosity in benezene of 0.0925. At a dosage of 0.005 grain per gallon of feedwater the total dissolved solids in the boiler water averaged 633 grains per gallon in two tests before carryover occurred.

EXAMPLE III

The material tested as an antifoam in this example was an addition product of alpha trioxymethylene and Polyglycol P–400 having an intrinsic viscosity in benzene of 0.0380. At a dosage of 0.005 grain per gallon of feedwater the total dissolved solids in the boiler water averaged 789 grains per gallon in two tests before carryover occurred.

EXAMPLE IV

The material tested as an antifoam in this example was an addition product of alpha trioxymethylene and Polyglycol P–400 made with an additional quantity of trioxymethylene and having an intrinsic viscosity in benzene of 0.0368. At a dosage of 0.005 grain per gallon of feedwater the total dissolved solids in the boiler water averaged 648 grains per gallon in two tests before carryover occurred.

EXAMPLE V

The material tested as an antifoam in this example was an addition product of alpha trioxymethylene and Polyglycol P–400 having an intrinsic viscosity in benzene of 0.0462. At a dosage of 0.005 grain per gallon of feedwater carryover did not occur until the total dissolved solids in the boiler water had reached 872 grains per gallon.

EXAMPLE VI

The material tested as an antifoam in this example was an addition product of alpha trioxymethylene and Polyethylene Glycol 900. When dissolved in the boiler feedwater at a dosage of 0.005 carryover did not occur until the total dissolved solids in the boiler water had reached 3118 grains per gallon.

EXAMPLE VII

The material tested as an antifoam in this example was an addition product of alpha trioxymethylene with Polyethylene Glycol 600 and 1,5-pentane diol in the molar ratio of 0.1:0.05:0.05. When dissolved in the boiler feedwater at a dosage of 0.01 carryover did not occur until the total dissolved solids in the boiler water had reached 414 grains per gallon.

EXAMPLE VIII

The material tested as an antifoam in this example was an addition product of alpha trioxymethylene and Carbowax 1000 reacted in a molar ratio of 1:1. When dis-

solved in the boiler 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 2947 grains per gallon.

EXAMPLE IX

The material tested as an antifoam in this example was alpha trioxymethylene and Polyglycol P–1200 reacted in substantial equimolar proportions. The addition product was made up into a dry-appearing pulverized composition by mixing 3 parts by weight of the addition product with 1 part by weight of oleic acid, 1 part by weight of dipropylene glycol and grinding the resultant mixture with 95 parts by weight of a dry pulverized lignin derivative commonly used in boiler water treatment and made by desulfonation and partial depolymerization of sodium lignin sulfonate by treatment with aqueous alkali at high temperature. This material exhibits an excellent dispersing effect on the antifoam addition agents but neither it nor the oleic acid nor the dipropylene glycol themselves exert an antifoam effect in the boiler. The dry pulverized antifoam composition was added to the feedwater at a dosage of 0.167 grain per gallon resulting in a concentration of the antifoam addition product in the feedwater of 0.005 grain per gallon. This permitted a total dissolved solids concentration in the boiler of 875 grains per gallon before carryover occurred. When the same product was tested at a concentration of 0.0075 grain per gallon in the feedwater a total dissolved solids concentration of 956 grains per gallon was permitted before carryover occurred. At a dosage of 0.010 grain per gallon of the antifoam in the feedwater a total dissolved solids concentration in the boiler water before carryover occurred was 576 grains per gallon. At a dosage of 0.015 grain per gallon of the antifoam in the feedwater the total dissolved solids concentration in the boiler before carryover occurred averaged 493 grains per gallon.

EXAMPLE X

The antifoam material tested in this example was the addition product of alpha trioxymethylene with Polyethylene Glycol 300 and Polyglycol P–400 reacted in molar ratios of 0.10:0.05:0.05. This addition product exhibited such a pronounced antifoam efficiency that an accelerated test was used. In order to provide an accelerated test a feedwater (herein referred to as a 210 grain water) having the following composition, expressed in parts per million by weight, was used.

Calcium hardness (as $CaCO_3$)	178.0
Magnesium hardness (as $CaCO_3$)	185.0
Alkalinity (methyl orange) (as $CaCO_3$)	1,370.0
Sodium chloride (as NaCl)	334.0
Tannin extract, dry	51.0
Sodium sulfate (as Na_2SO_4)	1,950.0

The test procedure was otherwise the same as previously described for 70 grain water except that the carryover point was between 300 and 450.

When so tested at a dosage of 0.005 grain per galllon the previously described addition product permitted a total dissolved solids concentration of 6850 grains per gallon in the boiler water before carryover occurred.

The exact procedures used in preparing these compositions are subject to some variation. The following examples are given to illustrate the specific details of preparation of the compositions described in the previous examples.

EXAMPLE XI

The composition of Example I was prepared as follows.

One hundred (100) grams of Carbowax 1000 and 75 grams of Polypropylene Glycol 750 was treated with 3.0 grams of alpha trioxymethylene and 0.5 gram of ferric chloride in 150 ml. of benzene. The mixture was heated gently for five hours, avoiding refluxing during this period. The mixture was then heated more strongly so that the mixture refluxed. The refluxing was continued for several hours, at which time 1.1 ml. of water were removed from the reaction mixture. Another 3.0 grams of alpha trioxymethylene was then added and the above procedure repeated. Another 0.5 gram of alpha trioxymethylene was added and the mixture refluxed for 7 hours. At the end of this time 5.4 ml. of water was found in the trap, making a total of 6.5 ml. of water removed from the reaction mixture. The theoretical volume of water to be expected was 3.6 ml. The excess water must have condensed on the cold finger from the air in the room and run down into the trap.

The reaction mixture was refluxed with 2.0 grams of potassium acetate for several hours, filtered, and the solvent removed under reduced pressure on the steam bath. The viscous dark brown liquid thus obtained solidified to a soft wax-like consistency on cooling.

Three grams of this solid was ground thoroughly with 97 grams of desulfonated and partially depolymerized sodium lignin sulfonate in a mortar and passed through a 60 mesh screen.

EXAMPLE XII

The composition of Example II was prepared as follows.

100 grams (0.1 mol) of Polyethylene Glycol 1000, 75 grams (0.1 mol) of Polypropylene Glycol 750, 5.4 grams (0.18 mol) of alpha trioxymethylene, 0.5 gram of ferric chloride and 150 grams of benzene are heated just below reflux point for one day (7 hours). The mixture was then refluxed until ½ of the theoretical amount of water was removed. 0.5 gram of alpha trioxymethylene was added, heated mildly for some hours and then additional amount of water was removed. Three more 0.5 gram portions were added as above until the theoretical amount of water was removed (3.6 cc.). 1 gram of potassium acetate was then added and the mixture refluxed for one hour. The solution was filtered while hot and the benzene removed with vacuum on a steam cone. The product was a soft brown waxy solid, which melted somewhat at higher than room temperature.

EXAMPLE XIII

The composition of Example III was prepared as follows:

160 grams (0.4 mol) of Polyglycol P–400, 9.6 grams (0.32 mol) of alpha trioxymethylene, 0.5 gram stannic chloride and 160 grams benzene were heated and treated in the same manner as described in Example XII. Seven additional 0.5 gram portions of alpha trioxymethylene were added and approximately 90% of the amount of water theoretically produced by the reaction was removed. The product was neutralized with 2 grams of potassium acetate and recovered as described in Example XII. The product was a viscous liquid.

EXAMPLE XIV

The composition of Example IV was prepared as described in Example XIII except that eight additional 0.5 gram portions of alpha trioxymethylene were added and 96% of the water theoretically formed was removed. This product was also a viscous liquid.

EXAMPLE XV

The product of Example V was prepared as described in Example XIII except that 0.5 gram of aluminum chloride was used in place of the stannic chloride and there were six 0.5 gram additions of alpha trioxymethylene. The amount of water removed was 86% of that theoretically formed. This product was also a viscous liquid.

EXAMPLE XVI

The composition tested as described in Example VI was prepared from the following ingredients:

40 grams of Polyethylene Glycol 900 (0.044 mol)

2 grams of alpha trioxymethylene (0.067 mol)
0.2 gram of ferric chloride
70 ml. of benzene

The glycol, alpha trioxymethylene and ferric chloride were mixed with benzene and the benzene distilled, water separated and the benzene returned to the reaction zone. At 1 to 2 hour intervals three one gram additions of alpha trioxymethylene were made until the benzene solution was very viscous. The ferric chloride was neutralized by potassium acetate and the benzene was removed under vacuum. The product was a brittle solid.

EXAMPLE XVII

The composition tested as described in Example VII was prepared from the following components:

30 grams Polyethylene Glycol 600 (0.05 mol)
5.2 grams 1,5-pentanediol (0.05 mol)
3.0 grams alpha trioxymethylene (0.10 mol)
0.2 gram ferric chloride
70.0 ml. benzene

The glycol, pentanediol, alpha trioxymethylene and ferric chloride were mixed in the benzene and the benzene was distilled, the water separated, and the benzene returned to the reaction zone until 1.8 ml. of water was collected. The ferric chloride was neutralized with potassium acetate and benzene was removed under vacuum. The product was a viscous liquid.

EXAMPLE XVIII

The composition tested as described in Example VIII was prepared from the following components:

50 grams of Carbowax 1000 (0.05 mol)
1.5 grams of alpha trioxymethylene (0.05 mol)
0.2 gram of ferric chloride

The Carbowax, alpha trioxymethylene and ferric chloride were mixed and heated at 80° C. under vacuum with a slow stream of air being bled through the reaction mixture. After two days of heating a very viscous liquid resulted. The ferric chloride was neutralized with potassium acetate. The product was a tan, hard solid.

EXAMPLE XIX

The composition tested as described in Example IX was prepared from the following components:

40 grams of Polyglycol P–1200 (0.033 mol)
1 gram of alpha trioxymethylene (0.033 mol)
0.2 gram of aluminum chloride (anhydrous)
50 ml. benzene

The glycol, alpha trioxymethylene and the aluminum chloride were mixed with benzene. The benzene was distilled. The water that distilled with the benzene was separated and the benzene was returned to the reaction zone. When 0.6 ml. of water had been collected, the aluminum chloride was neutralized with potassium acetate. The solution was filtered and the benzene was removed under vacuum on the steam cone. The product was a thin liquid.

EXAMPLE XX

The composition tested as described in Example X was prepared from the following components:

15 grams of Polyethylene Glycol 300 (0.05 mol)
20 grams of Polyglycol P–400 (0.05 mol)
3 grams of alpha trioxymethylene (0.10 mol)
0.2 gram of ferric chloride
70 ml. of benzene

The two glycols, the alpha trioxymethylene and the ferric chloride were mixed with the benzene. The benzene was distilled and the water distilling with the benzene was separated and the benzene returned to the reaction zone. When 1.8 ml. of water had been collected, the ferric chloride was destroyed with potassium acetate and the solution was filtered. The benzene was removed under vacuum at steam temperatures. The product was a viscous liquid.

In the foregoing examples the so-called "Polyethylene Glycols" followed by a number are the trade names for products made by Carbide and Carbon Chemicals Corporation having the general formula:

$$HOCH_2(CH_2OCH_2)_xCH_2OH$$

"Polyethylene Glycols" 300, 600 and 900 are all viscous light colored somewhat hygroscopic liquids of low vapor pressure having molecular weights from 300 to 900. The "Carbowax" compounds are polyoxyethylene glycols which are wax-like solids having a molecular weight above 1000. The number following the name "Carbowax" indicates the approximate molecular weight.

The Polyglycol P compounds are commercial polyoxypropylene glycols made by Dow Chemical Company. The number following the letter "P" signifies the average molecular weight of the glycols present in the mixture. For example, Polyglycol P–400 consists mainly of a mixture of hexaoxypropylene glycol

$$[HO(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_6H]$$

and heptaoxypropylene glycol

$$[HO(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_7H]$$

The addition products employed for the purpose of the invention may also be prepared by reacting the aldehyde with a polyoxyalkylene glycol in which the oxyalkylene groups contain both oxyethylene and 1,2-oxypropylene groups in the same molecule. Compounds of this type are described in U. S. Patent 2,425,845 and are sold under the trade name "Ucon." Typical materials of this type which can be reacted with formaldehyde to produce addition products suitable for the practice of the present invention are Ucon 75 H 1400, Ucon 75 H 4900, Ucon 75 H 9150, and Ucon 75 H 90,000 (Carbide and Carbon Chemicals Corporation). The preferred materials of this type are the polyoxyalkylene glycols in which the oxyalkylene groups consist of oxyethylene and 1,2-oxypropylene groups in an approximate weight ratio within the range of 3:1 to 1:9.

The products of the invention are preferably prepared by reacting substantially equal mol quantities of the glycol and formaldehyde. If an excess of formaldehyde is used, part of it distils.

Where reference is made herein to molecular weights of compounds of the class described it will be understood that these are determined by the Zerewitinoff method of measuring active hydrogen. The apparatus described by Kohler, Stone and Fuson, "Journal of the American Chemical Society," vol. 49, page 3181 (1927), can be used in the determination of the active hydrogen.

The addition products referred to herein can also be described in terms of their intrinsic viscosity. Intrinsic viscosity is defined as the limiting value of the specific viscosity divided by concentration, as concentration approaches zero. Specific viscosity is defined as follows:

$$\eta_{sp}=(\eta_c-\eta_o)/\eta_o$$

where η_c and η_0 are the viscosities of a solution of the polymer at a concentration, c, and the viscosity of the solvent, respectively. Intrinsic viscosity is then expressed mathematically as

$$(\eta)-\left[\frac{\eta_{sp}}{c}\right]_{c=0}$$

and is readily obtained by determining η_{sp} at several values of concentration, c, plotting the experimental values of

$\eta_{sp/c}$ for the various values of c against c; and extrapolating to $c=0$, whereby (η) is obtained.

By the determination of intrinsic viscosity for a series of polymer mixtures, differing only in average polymer size, it has been found that where n in the formula is 2 and x is 23, the intrinsic viscosity in benzene should be greater than 0.135. When n is 3 (the "larger" oxyalkylene groups are 1,2-oxypropylene) and x is 7, the intrinsic viscosity in benzene should be greater than 0.040. When n is both 2 and 3 (e. g., the polymers contain oxyethylene groups and oxypropylene groups in a weight ratio of approximately 1:1 and x had an average value of approximately 19) the intrinsic viscosity in benzene should be greater than 0.100.

The products hereinabove described may be liquid or low-melting wax-like solids, and in some cases may be rather hard solids which may be pulverized by grinding. They 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 above. 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 percent 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 addition products 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.

In general where the addition product is incorporated with tannins, sodium lignin sulfonate and desulfonated lignins prior to adding it to the boiler feedwater, the quantity of the addition product 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 97% 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 addition products 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 addition products. 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 antifoam ingredients 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 addition products.

Table I

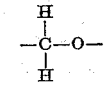
Magnesium, Grains Per Gallon in Boiler Water (Expressed as $CaCO_3$)	Tannins, Sodium Lignin Sulfonate and/or Desulfonated Lignins Grains per Gallon in Boiler Water
0	0
1–5	0. 5–1
5–10	1–2
10–20	2–3

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

The present application is a continuation-in-part of my copending application Serial No. 224,250, filed May 2, 1951, now abandoned, which in turn was a continuation-in-part of my application Serial No. 123,103, filed October 22, 1949, now abandoned.

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 a polyoxyalkylene diol having a plurality of interconnected oxyalkylene groups, each containing 2 to 10 carbon atoms, interlinked with a sufficient number of



groups to produce a diol having an average molecule weight within the range of 1000 to 11,500 and having hydroxyl groups attached to terminal carbon atoms, said diol being substantially insoluble in said boiler water at the temperature of steam generation, the quantity of said diol 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 which comprises dispersing in said water a quantity of a compound having the following general formula

$$HO[(C_nH_{2n}O)_xCH_2O]_y(C_nH_{2n}O)_xH$$

wherein n is an integer from 2 to 3, x and y are integers, the average molecular weight is within the range from 1000 to 11,500 and the compound is substantially insoluble in said boiler water at the temperature of steam generation, the quantity of said compound being effective to inhibit the tendency of said water to foam on boiling, and heating the resultant 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 addition product of alpha-trioxymethylene and a polyoxyalkylene glycol having two terminal hydroxyl groups spaced by at least 4 carbon atoms and in which the oxyalkylene groups contain 2 to 5 carbon atoms, said addition product having a molecular weight within the range of 1000 to 11,500 and 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.

4. 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 alpha-trioxymethylene, a polyoxyethylene glycol having two terminal hydroxyl groups spaced by at least 4 carbon atoms and having a molecular weight of approximately 300 and a polyoxypropylene glycol having a molecular weight of approximately 400 reacted in a molar ratio of approximately 2:1:1 and 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.

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 alpha-trioxymethylene and polyoxypropylene glycol having two terminal hydroxyl groups spaced by at least 4 carbon atoms and having a molecular weight of at least 400 reacted in approximately equimolar proportions and 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 boiler water 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, a quantity of a foam inhibiting compound corresponding to from 0.001 grain to 0.1 grain of said compound per gallon of said water, said compound being an addition product of alpha-trioxymethylene and a polyoxyalkylene glycol having two terminal hydroxyl groups separated by at least 4 carbon atoms and in which the oxyalkylene groups contain 2 to 5 carbon atoms, said addition product having a molecular weight within the range of 1000 to 11,500 and 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.

7. A boiler water 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, a quantity of a foam inhibiting compound corresponding to from 0.001 grain to 0.1 grain of said compound per gallon of said water, said compound being an addition product of alpha-trioxymethylene and polyoxyethylene glycol having two terminal hydroxyl groups separated by at least 4 carbon atoms and having a molecular weight of approximately 1000 reacted in a molar ratio of approximately 1:1 and 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.

8. A boiler water 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, a quantity of a foam inhibiting compound corresponding to from 0.001 grain to 0.1 grain of said compound per gallon of said water, said compound being an addition product of alpha trioxymethylene and polyoxypropylene glycol having two terminal hydroxyl groups separated by at least 4 carbon atoms and having a molecular weight of at least 400 reacted in approximately equimolar proportions and 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.

9. A boiler water 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, a quantity of a foam inhibiting compound corresponding to from 0.001 grain to 0.1 grain of said compound per gallon of said water, said compound being an addition product of alpha-trioxymethylene, a polyoxyethylene glycol having a molecular weight of approximately 300 and a polyoxypropylene glycol ahving a molecular weight of approximately 400 reacted in a molar ratio of approximately 2:1:1, said glycols having two terminal hydroxyl groups separated by at least 4 carbon atoms and said compound 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.

10. An antifoam composition for minimizing the production of foam in the generation of steam from water containing magnesium compounds which comprises essentially 0.5% to 12% by weight of an addition product of alpha-trioxymethylene with a polyoxyalkylene glycol having two terminal hydroxyl groups spaced by at least 4 carbon atoms and in which the oxyalkylene groups contain 2 to 5 carbon atoms, said addition product having a molecular weight of at least 1000 and being substantially insoluble in boiler water at steam generating temperatures, and approximately 50% to 97% by weight of a substance from the group consisting of tannins, sodium lignin sulfonate and desulfonated lignins.

11. An antifoam composition for minimizing the production of foam in the generation of steam from water containing magnesium compounds which comprises essentially 0.5% to 12% by weight of a compound having the following general formula

$$HO[(C_nH_{2n}O)_xCH_2O]_y(C_nH_{2n}O)_xH$$

wherein n is an integer from 2 to 3, x and y are integers, the average molecular weight is within the range from 1000 to 11,500 and the compound is substantially insoluble in boiler water at steam generating temperatures, and ap-

proximately 50% to 97% by weight of a substance from the group consisting of tannins, sodium lignin sulfonate and desulfonated lignins.

12. An antifoam composition for minimizing the production of foam in the generation of steam from water containing magnesium compounds which comprises essentially 0.5% to 12% by weight of a polyoxyalkylene diol having a plurality of interconnected oxyalkylene groups, each containing 2 to 10 carbon atoms, interlinked with a sufficient number of oxymethylene groups to produce a diol having an average molecular weight within the range of 1000 to 11,500 and having hydroxyl groups attached to terminal

carbon atoms, said diol being substantially insoluble in boiler water at steam generating temperatures, and approximately 50% to 97% by weight of a substance from the group consisting of tannins, sodium lignin sulfonate and desulfonated lignins.

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