The present invention relates to antifoaming compositions which are used in steam boilers and similar steam generators, evaporators, etc., to overcome the tendency of the water therein to foam and hence to bring about the priming of the steam generator or the like.

This application is a continuation-in-part of our co-pending application Serial No. 436,488, filed March 27, 1942, now abandoned.

It is well known in the operation of steam boilers, such as in electric power plants, railroad locomotives and the like, or in evaporators, that the water therein, even though initially it shows very little tendency to foan will, when the amount of total solids therein approaches a relatively high concentration, develop a very decided tendency to foam. When this occurs, considerable quantities of water are physically carried out of the boilers or evaporators with the steam, thus appearing in the steam lines and in the eventual condensate. Such priming has many disadvantages because it tends to contaminate the steam lines, to plug or corrode the valves, and under serious conditions may even impair the cylinders and piston rods of the steam engines, or the impeller blades of turbines in which the steam is used for the generation of power.

Attempts have been made in the past to control this foaming, by excessive blowdown of the boilers or by the injection thereinto of such materials as castor oil, tallow, and the like. While these fatty materials 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 acids or glycerides are unstable under the conditions existing in the boilers, particularly as the pressure and temperature increase, the high temperatures leading to rapid decomposition of the glycerides, which, if anything, will tend to increase the foaming and priming difficulties. 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-distil out of the boilers, thus appearing in the steam and in the condensate. This, of course, is highly undesirable. Furthermore, since these types of antifoaming agents usually 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 those which have a tendency to decompose do so quite rapidly, and hence their effectiveness is of short duration, which therefore necessitates the continual charging into the boilers or other steam generators of relatively large amounts of these older antifoaming agents. Moreover, such antifoaming agents are difficult to use because the amounts in which they are efficacious are very critical, and any over dosage usually aggravates the difficulty instead of curing it.

One of the objects of the present invention is the preparation of a liquid suitable for the generation of steam in steam generators and comprising water containing dispersed therein a very small amount of a specific type of compound whereby, when such water is heated to the boiling point in a steam boiler or other generator, being thereby evaporated, the concentration of solids therein will not bring about excessive foaming and the resulting priming, the added compound being substantially non-volatile with the steam and stable, so that it will be retained by the water and neither its decomposition products will appear in the steam and the resulting condensation thereof. Other objects will appear hereinafter.

In accordance with the invention it has been discovered that there is a series of compounds which may be broadly designated as unsymmetrically diacylated polynitines where one acyl group is a long chain aliphatic acyl group and the other is a short chain aliphatic acyl group, which are useful as antifoaming and antipriming agents in steam generators under superatmospheric pressure conditions.

The compounds involved in the practice of the present invention can be illustrated by the structural formula:

\[ X-C-N-Y-N-C-Z \]

in which \( X \) and \( Z \) each represents an aliphatic hydrocarbon or hydroxy aliphatic hydrocarbon group, \( Y \) is the residue from a polynitine selected from the group consisting of monoalkyleneamines and polyalkylene polynitines, one of said radicals \( X \) and \( Z \) containing at least about 15 carbon atoms and the other not more than about 8 carbon atoms, and the total number of carbon atoms in said dialkyl compound being at least 18, where the polynitine is a monoalkylene diamine and at least 22 carbon atoms where the polynitine is a polyalkylene polynitine. Examples of these dialkyl compounds derived from alkylenediamines such as ethylene diamine or decamethylene diamine are the acetyl-stearyl derivatives, butyryl-palmityl derivatives and the acetyl-erucyl deriva-
Examples of these unsymmetrical compounds derived from polyalkylene polyamines, e.g., diethylene triamine, triethylene tetramine and tetraethylene pentamine are the acetyl-stearyl derivatives, the butyryl-palmityl derivatives and the acetyl-crotyl derivatives. The range of carbon atoms in these compounds is preferably within the range of 18 to 32 carbon atoms.

We shall describe hereinafter the preparation of several of the materials, and while the examples disclose a few of many satisfactory preparative procedures, in most cases the same product may be obtained by more than one route.

The most-used method of preparation involved the use of the acid and the amine, in nearly theoretical amounts for the product desired, and consisted essentially in the initial formation of the amine salt of the acid, followed by dehydration to the monoamidine by heating. The second acid was then added and the process continued to give the desired unsymmetrical diamide. In certain cases, the use of the acid halide was resorted to in order to introduce an acyl group. In still another very useful procedure, the fatty acid ester was used instead of the acid itself. Thus, while the ester can, for example, as methyl, ethyl, glycol, etc., the glycerides of the high molecular weight acids are often very readily obtainable and were the subject of much of the preparative work. By heating the glyceride and the polyamine together in the proper proportions, the alkaline amine causes the ester to be split, liberating the fatty acid, which then reacts with the amine to give the amide.

Usually when using the triglycerides, such proportions were used that two of the three acid chains would be split off from the ester and used, and the remaining fatty acid monoglyceride remained in the product as a harmless by-product. However, excellent materials have also been formed where the proportion of triglyceride or other ester used was such that all the available acyl chains were used in forming the amide. Indeed, the reaction of theoretical amounts of a polyethylene polyamine and a glycerol monostearate has yielded useful products.

The number of different compounds which can be prepared is quite numerous, and while we are giving a large number of examples, we do not wish to be limited to those specifically described nor to the species claimed. These examples are:

Example I
A mixture of 13.9 grams of commercial stearic acid and 5 grams of a 60% aqueous solution of ethylene diamine was stirred at 150 degrees C. to 160 degrees C. for 1.5 hours, after which 3.9 grams of acetyl chloride was cautiously added and heating continued for 10 to 15 minutes. When cool, the product was a light brown wax.

Example II
The product of Example I was also made by a slightly different procedure. Instead of the addition of acetyl chloride, 3 grams of acetic acid was added and heating of the mixture at 150 degrees C. to 160 degrees C. continued for 2 hours further.

Example III
A mixture of 12.8 grams of palmitic acid and 5 grams of a 60% aqueous solution of ethylene diamine was stirred at 150 degrees C. to 160 degrees C. for 4 hours. At 120 degrees C., 3.9 grams of acetyl chloride was then added cautiously and the temperature restored to 150 degrees C. to 160 degrees C. for 15 to 20 minutes. When cool, the product was a tan wax.

Example IV
A mixture of 14.1 grams of oleic acid and 7.3 grams of triethylene tetramine was heated with stirring at 150 degrees C. to 160 degrees C. for 1.5 hours. The reaction mixture was then cooled to room temperature and 3.9 grams of acetyl chloride was then added dropwise with stirring. The temperature was allowed to rise to 110 degrees C. and maintained there by the use of external heat for about 30 minutes, when the reaction was considered complete. The product, when cool, was a soft, brown wax and had no odor of acetic acid.

Example V
A mixture of 7.4 grams of an 85% aqueous solution of lactic acid and 10.2 grams of triethylene tetramine was heated with stirring at 150 degrees C. to 160 degrees C. for 2 hours. Then 18.8 grams of stearic acid was added and the process continued another 2 hours. When cool, the product was a brown wax.

Example VI
A mixture of 0.3 grams of alpha-hydroxyisobutyric acid and 8.8 grams of triethylenetetramine was heated with stirring at 150 degrees C. to 160 degrees C. for 2 hours. Then 10.2 grams of stearic acid was added and the process continued another 2 hours. When cool, the product was a tan wax.

Example VII
A mixture of 5.2 grams of diethylene triamine and 12.8 grams of palmitic acid was heated with stirring at 150 degrees C. to 160 degrees C. for 2 hours. Then 3.9 grams of acetyl chloride was added gradually at 120 degrees C. and the reaction completed by heating for a short time. When cool, the product was a brown wax.

The products hereinabove described, while not ordinarily corrosive as soluble in water to any great extent, may be suitably dispersed in water or emulsified therefrom, so that effective amounts thereof may be introduced and be present in the water within the steam generator under operating conditions. The emulsifying or dispersing agent used must, however, be of a kind that does not cause foaming, either by itself or by its decomposition products. The compounds may be used conjointly with each other as well as with other known antifoaming agents, such as, for example, castor oil.

The amounts of these high molecular weight diacyl derivatives of polyamines which are required are extremely small, and in general one gram per gallon is ample. For many purposes, however, amounts of as little as 0.01 gram per gallon in the feed water will still give valuable results, and the amounts may be even further reduced. For example, 0.06 gram per gallon of this type of condensation product will suppress foam in a boiler for from 15 to 20 minutes. Comparing this with the efficiency of castor oil used on the order of 0.1 gram per gallon, which will suppress the foam for only about 30 seconds to one minute, it is obvious that if one were to use castor oil it would have to be continuously fed into the boiler, with an unavoidable accumulation in the boiler of a lot of soap produced by the reaction of the liberated fatty acids with the alkali present in the water, which would only aggravate the problem. The diacyl derivatives under discussion,
however, are quite stable and do not yield undesirable by-products.

Depending, of course, upon the degree of concentration of solids, the dosage may be varied, but one grain per gallon is about as much as would ever be used even under serious conditions, and for many purposes 500 grain per gallon and even less can be used. The process is particularly effective at pressures of about 250 pounds per square inch.

The introduction of the antifoaming compounds of the present invention into the boiler may be accomplished in a number of ways. Thus, the antifoaming compositions may be blended or physically mixed with, say, sodium carbonate or some other material used for creating the boiler water and pumped with the feed water into the boiler by means of either an injector or a feed water pump. The compounds may also be dissolved in suitable organic water-miscible solvents such as alcohols, ethers, ketones, etc., and introduced in small measured amounts into the feed water entering the boiler. Suitable mechanical measuring devices which will periodically or continuously inject the required dosage of antifoaming compounds into the feed water may be used, so that the introduction will be more or less in proportion to the steam consumption to which the steam generator is subjected. Another manner of introducing the antifoaming compositions is to form an emulsion thereof in water and then feed said emulsion either directly into the boiler or the feed water lines leading to it.

The preferred active antifoam ingredients are oily to waxy substantially water insoluble substances characterized by stability in hot aqueous alkaline liquids such as are used in locomotive boilers and under the conditions which are present in locomotive boilers. Compositions prepared in accordance with the invention have been demonstrated to be particularly effective in locomotive boilers under superatmospheric pressure conditions, within the range of 150 to 500 pounds per square inch and the corresponding temperature conditions. Tests have demonstrated that these compositions are effective even at the much higher pressure and temperature conditions in stationary boilers for power plant operations, as, for example, superatmospheric pressures up to 1500 pounds per square inch.

Apart from the fact that the preferred active antifoam ingredients function under severe conditions where other so-called antifoam materials are ineffective, the reason for the functioning of these materials is not known. It has been proven in tests connected with the practice of this invention that these materials are very stable to hydrolysis as compared with many other different types of compounds.

The amounts of antifoam agent employed in inhibiting foam will depend upon several factors among them the conditions under which the foam occurs, the amount of foam suppression desired, the per cent of solids in the foaming liquid, the alkalinity, temperature, and pressure of the foaming liquid, the type and degree of agitation, and the kind of gas present in the gas phase of the foam. It is, therefore, impossible to state any rigid rules for estimating the amount of an antifoam which needs to be used. In general, the antifoam will be added in relatively small amounts, gradually increasing in size, until the foam is controlled to the extent desired.

In the prevention of priming in a power plant or locomotive boiler operating at ordinary pressures, e.g., 250 pounds per square inch, it has been found that the effective antifoam compositions of this invention, i.e., those possessing the requisite molecular size for this use, as explained above, are efficient when they are introduced into the feed water at a concentration of the order of magnitude of 0.01 grain per gallon, based on the weight of active antifoam ingredient. Thus, a boiler operating at 10 concentrations, which is not unusual, would have 0.1 grain of active antifoam per gallon of boiler water. Some foam suppression has been obtained with only 8 parts by weight of the active ingredient per billion of water in the feed water going to a boiler. Quantities of from 125 to 500 parts by weight of the active ingredient per billion of water are frequently sufficient merely to improve steam quality. Such proportions have allowed some users to operate with increased dissolved solids of as much as 15% over the amount permissible without the steam conditioner. Having thus described the invention, what we claim as new and desire to secure by Letters Patent of the United States is:

1. A method of generating steam which comprises boiling, under superatmospheric pressure conditions, water containing an amount of total dissolved solids tending to produce foaming and priming and a quantity of acetyl stearyl ethylene diamine, said quantity being sufficient to substantially inhibit said foaming and priming.

2. A method of generating steam which comprises boiling, under superatmospheric pressure conditions, water containing an amount of total dissolved solids tending to produce foaming and priming and a quantity of acetyl triethylene tetramine, said quantity being sufficient to substantially inhibit said foaming and priming.

3. A method of generating steam which comprises boiling, under superatmospheric pressure conditions, water containing an amount of total dissolved solids tending to produce foaming and priming and a quantity of palmityl acetyl diethylene triamine, said quantity being sufficient to substantially inhibit said foaming and priming.

4. A method of generating steam from a boiler water having a tendency to foam on boiling which comprises dispersing into said water an asymmetrical diacylated polyamine in which each acyl radical has a different number of carbon atoms, one of said acyl radicals being derived from a short chain monocarboxylic acid from the group consisting of fatty acids and hydroxy fatty acids containing 2 to 4 carbon atoms and the other containing 2 to 4 carbon atoms, said diacylated polyamine being dispersed into said water in an amount sufficient to substantially inhibit the tendency of said water to foam on boiling, and boiling said water.

5. A method of generating steam from a boiler water having a tendency to foam on boiling which comprises dispersing into said water an asymmetrical diacylated ethylenediamine in which each acyl group has a different number of carbon atoms, one of said acyl groups being derived from a fatty acid containing 2 to 4 carbon atoms and the other being derived from a fatty acid containing at least 14 carbon atoms, said diacylated diamine being dispersed in said water in an amount sufficient to substantially inhibit said foaming and priming.
sufficient substantially to inhibit the tendency of said water to foam on boiling, and boiling said water.

6. A method of generating steam from a boiler water having a tendency to foam on boiling which comprises dispersing into said water an unsymmetrical diacylated polyamine in which each acyl group has a different number of carbon atoms, one of said acyl groups being derived from a fatty acid containing 2 to 4 carbon atoms and the other being derived from a fatty acid containing at least 14 carbon atoms, and the polyamine being a polyethylene polyamine containing at least 3 nitrogen atoms and 4 to 8 carbon atoms, said diacylated polyamine being dispersed into said water in an amount sufficient substantially to inhibit the tendency of said water to foam on boiling, and boiling said water.

7. A method of generating steam from a boiler water having a tendency to foam on boiling which comprises dispersing into said water lactyl steryl triethyleneetetramine in an amount sufficient substantially to inhibit the tendency of said water to foam on boiling, and boiling said water.

8. A method of generating steam from a boiler water having a tendency to foam on boiling which comprises dispersing into said water alpha-hydroxy isobutyryl steryl triethyleneetetramine in an amount sufficient substantially to inhibit the tendency of said water to foam on boiling, and boiling said water.

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