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PREVENTION OF FOAMING IN STEAM GENERATION

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14 Claims. (Cl. 252—321)

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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.

One of the objects of the present invention relates to a liquid suitable for the generation of steam in steam generators and comprising water containing a very small quantity of particular kinds of N,N'-disubstituted diamides of complex dibasic acids, 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, these compounds being substantially nonvolatile with the steam, and stable, so that they will be retained by the water and neither they nor their decomposition products will appear in the steam and the resulting condensation thereof.

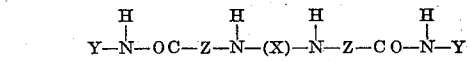
It is well known in the operation of steam boilers, such as in electric power plants, railroad locomotives and the like, or in evaporators, that the water therein, even though initially it shows very little tendency to foam, will, when the amount of total solids therein approaches a relatively high concentration, 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 temperatures increase, the high temperatures leading to rapid decomposition of the glycerides, which, if any thing, will tend to increase the foaming and priming difficulties. Furthermore, in many instances certain of the

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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 also very undesirable. Furthermore, such 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 overdosage usually aggravates the difficulty instead of curing it.

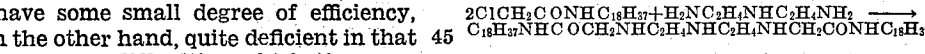
Applicant has now discovered, however, that there is a series of compounds, which may be designated as N,N'-disubstituted diamides of complex dibasic acids, which are of a high order of efficiency when used as an antifoaming and antipriming agent in steam generators.

The materials of this invention may be represented by the general formula



wherein Y is an aliphatic radical of relatively large moleculuar size; Z is the divalent hydrocarbon radical of a halogeno-acid; and X is the residue from an organic polyamine, whose terminal nitrogen atoms appear on either side of X in the above formula.

An example of a compound represented by the above formula is N,N'-diethylenetriaminobis-N-octadecylacetamide, obtained by the reaction of two mols of N-octadecylchloroacetamide and one of diethylenetriamine according to the following equation:



In order to yield an efficient antifoam material, it appears to be necessary that the alkyl groups, Y, of the formula containing at least about 14 carbon atoms each but the radicals Z may be varied within wide limits, such halogeno-acids as chloroacetic, beta-chlorobutyric, and o-iodobenzoic being all suitable as starting materials in the preparation of the N-alkylated amides. Furthermore, the nature of the organic polyamine, the residue of which is repre-

sented by X in the formula, may be varied considerably. Thus, coupling has been effected by means of such amines as hydrazine, piperazine, the polyalgylenepolyamides, alkylenediamines, and the phenylenediamines, yielding efficient products in every case. Obviously, in the case where hydrazine is the coupling agent, the (X) of the general formula will be absent. Also, the alkyl groups on the amido nitrogens may be derived from either primary or secondary amines. It is to be understood that the formulas recited in the specification and claims are "probable" in that the formulas given are believed to be possessed by the compounds disclosed, or whose method of preparation is disclosed, in this specification.

The simplest method of manufacturing the materials of this invention involves the initial formation of the N-alkylated amide of the halogeno-acid by merely heating the desired amine with the halogeno-acid (or corresponding acid halide), and the subsequent coupling of the product by introducing the polyamine and heating until the halogen groups of the halogeno-acid have been aminated. This method is illustrated in the following examples of the preparation of materials possessing value as antifoam agents, but it is to be understood that I do not wish to be limited by the examples.

Example 1.—A mixture of 13.6 grams (0.04 mol) of N-octadecylchloroacetamide and 2.1 grams (0.02 mol) of diethylenetriamine was stirred 2 hours at 150–160° C.

Example 2.—A mixture of 12 grams (0.033 mol) of N-octadecylchloroacetamide and 2 grams (0.016 mol) of 40% aqueous hydrazine hydrate was stirred for 3 hours at 150–160° C., after a brief initial period at a lower temperature to prevent excessive frothing.

Example 3.—To 0.05 mol of N-octadecylchloroacetamide at 150–160° C., 2.2 grams (0.025 mol) of 68% aqueous ethylenediamine was added dropwise with stirring, and stirring and heating continued 3 hours.

Example 4.—To 0.05 mol of N-octadecylchloroacetamide at 150–160° C., 5 grams (0.025 mol) of piperazine hexahydrate was added with stirring, and the stirring and heating continued for 2 hours.

Example 5.—To 0.05 mol of N-octadecylchloroacetamide at 150–160° C. was added 2.7 grams (0.025 mol) of m-phenylenediamine with stirring, and stirring and heating were then continued 2 hours longer.

Example 6.—To 0.05 mol of N-octadecylchloroacetamide at 150–160° C. was added 3.7 grams (0.025 mol) of triethylenetetramine with stirring, and stirring at 150–160° C. was then continued 2 hours longer.

Example 7.—To 0.05 mol of N-octadecylchloroacetamide at 150–160° C. was added with stirring, dropwise and simultaneously, 3 grams (0.03 mol) of ethylene dichloride and 3 grams (0.03 mol) of diethylenetriamine. The mixture was then stirred at 150–160° C. for 2 hours longer. It is believed that by this procedure, two molecules of the alkylated chloroacetamide are joined through an amine-containing linkage represented by a large polyalkylenepolyamine.

Example 8.—To 0.005 mol of N-tetradecylchloroacetamide at 150–160° C. was added 0.26 grams (0.0025 mol) of diethylenetriamine, with stirring, and then stirring at 150–160° C. was continued 2 hours longer.

Example 9.—A mixture of 2.5 grams of beta-chlorobutyric acid and 6.34 grams of octadecylamine (with a mean molecular weight of 264) was stirred 2 hours at 150–160° C. Then 1.4 cc. of diethylenetriamine was added and the mixture stirred 3 hours longer at 150–160° C.

Example 10.—A mixture of 5 grams of beta-chloropropionyl chloride and 6.7 grams of octadecylamine (with a mean molecular weight of 264) was made at room temperature, and quickly warmed itself to a homogeneous liquid mass, which was gradually heated, with stirring, to 150° C. Then 1.4 cc. of diethylenetriamine was added and the mixture stirred 3 hours at 150–160° C.

Example 11.—10.6 grams of octadecylamine (having a mean molecular weight of 264) was added portion-wise to a melt of 10.7 grams of o-iodobenzoyl chloride, and the mixture brought to 150° C. with stirring. Then 2.16 cc. of diethylenetriamine was added and the mixture stirred 2 hours at 150–160° C.

These compounds, while not ordinarily considered as soluble in water to any great extent, may be suitably dispersed in water or emulsified therewith, 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 the compounds hereinabove described which are required are extremely small, and in general one grain per gallon is ample. For many purposes, however, amounts of as little as $^1/_{100}$ grain per gallon in the feed water will still give valuable results, and the amounts may be even further reduced. 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 have to be used even under serious conditions, and for many purposes $^1/_{100}$ 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 dispersed or physically mixed with, say, sodium carbonate or some other material used for treating 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 the anti foaming 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 compounds 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 invention therefore is not to be limited by the manner of introduction of the anti-foaming composition but rather is to be construed in the terms of the hereunto appended claims.

I claim:

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 the condensation product of about 2 mols of N-octadecylchloroacetamide and 1 mol of diethylenetriamine, 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 the condensation product of about 2 mols of N-octadecylchloroacetamide and 1 mol of hydrazine, 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 the condensation product of about 2 mols of a N-octadecylchloroacetamide and 1 mol of piperazine, said quantity being sufficient to substantially inhibit said foaming and priming.

4. 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 the condensation product of about 2 mols of an N-alkyl halogeno organic acid amide and 1 mol of an organic polyamine having at least two amino groups with replaceable hydrogen atoms, said amino groups being connected by a group containing not more than 6 carbon atoms and the N-alkyl group containing at least 14 carbon atoms, said quantity being sufficient to substantially inhibit said foaming and priming.

5. 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 a compound having the following general formula

Y-NH-OC-Z-NH-(X)-NH-Z-CO-NH-Y

in which Y represents an aliphatic radical containing at least about 14 carbon atoms; Z is the divalent hydrocarbon radical of a halogeno-acid; and X is the residue from an organic polyamine whose terminal nitrogen atoms appear on either side of X in the above formula, the amino groups in said organic polyamine being separated by not more than 6 carbon atoms and said quantity being sufficient to substantially inhibit said forming and priming.

6. A liquid for the generation of steam substantially devoid of foaming and priming tendencies when heated to the boiling point, comprising water containing an amount of total dissolved solids tending to produce foaming and priming and a quantity of a condensation product of 2 mols of an N-alkyl halogeno organic acid amide and 1 mol of an organic polyamine having at least two amino groups with replaceable hydrogen atoms, said amino groups being connected by a group containing not more than 6 carbon atoms and the N-alkyl group containing at least 14 carbon atoms, said quantity being sufficient to substantially inhibit said foaming and priming.

7. A liquid for the generation of steam, substantially devoid of foaming and priming tendencies when heated to the boiling point, comprising water containing an amount of total dissolved solids tending to produce foaming and priming and a quantity of a compound having the following general formula

Y-NH-OC-Z-NH-(X)-NH-Z-CO-NH-Y

wherein Y is an aliphatic radical containing at least 14 carbon atoms; Z is the divalent hydrocarbon radical of a halogeno-acid; and X is the residue from an organic polyamine whose terminal nitrogen atoms appear on either side of X in the above formula, the amino groups in said organic polyamine being separated by not more than 6 carbon atoms and said quantity being sufficient to substantially inhibit said foaming and priming.

8. A liquid for the generation of steam, substantially devoid of foaming and priming tendencies when heated to the boiling point, comprising water containing an amount of total dissolved solids tending to produce foaming and priming and a quantity of the condensation product of about 2 mols of N-octadecylchloroacetamide and 1 mol of diethylenetriamine, said quantity being sufficient to substantially inhibit said foaming and priming.

9. 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 the condensation product of about 2 mols of an N-alkyl halogeno organic acid amide and about 1 mol of a polyethylene polyamine having two terminal primary amino groups, said N-alkyl group containing at least 14 carbon atoms, and said quantity being sufficient to substantially inhibit said foaming and priming.

10. A liquid for the generation of steam substantially devoid of foaming and priming tendencies when heated to the boiling point, comprising water containing an amount of total dissolved solids tending to produce foaming and priming and a quantity of the condensation product of about 2 mols of an N-alkyl halogeno organic acid amide and about 1 mol of a polyethylene polyamine having two terminal primary amino groups, said N-alkyl group containing at least 14 carbon atoms, and said quantity being sufficient to substantially inhibit said foaming and priming.

11. 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 the condensation product of about 2 mols of N-octadecylchoroacetamide and 1 mol of M-phenylenediamine, said quantity being sufficient to substantially inhibit said foaming and priming.

12. A liquid for the generation of steam substantially devoid of foaming and priming tendencies when heated to the boiling point comprising water containing an amount of total dissolved solids tending to produce foaming and priming and a quantity of the condensation product of about 2 mols of N-octadecylchloroacetamide and 1 mol of m-phenylenediamine, and said quantity being sufficient to substantially inhibit said foaming and priming.

13. 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 a condensation product of about 2 mols of N-octadecylchloroacetamide and 1 mol of triethylenetetramine, said quantity being sufficient to substantially inhibit said foaming and priming.

14. A liquid for the generation of steam substantially devoid of foaming and priming tendencies when heated to the boiling point comprising water containing an amount of total dissolved solids tending to produce foaming and priming and a quantity of the condensation product of about 2 mols of N-octadecylchloroacetamide and 1 mol of triethylenetetramine, and said

quantity being sufficient to substantially inhibit said foaming and priming.

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