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PROCESS OF MINIMIZING THE PRODUCTION OF FOAM IN STEAM GENERATORS

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The present invention relates to compositions and methods to reduce or prevent foaming of liquids.

One of the objects of the present invention is to provide a liquid suitable for the generation of steam in steam generators, and comprising water containing dissolved therein a very small amount of sulfonamide, 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 or priming resulting therefrom. The compounds incorporated in the water are substantially non-volatile with steam and are stable, so that they will be retained by the water, and neither they nor their decomposition products will appear in the steam or in the condensate thereof.

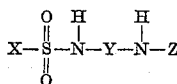
It is well known in the operation of steam boilers, such as in electric power plants, railroad locomotives, and the like, or in evaporators, that the water therein, even though initially it shows very little tendency to foam, will, when the amount of total solids therein approaches a relatively high 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 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 therinto 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

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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 broadly designated as sulfonamides, which are of a high order of efficiency when used as antifoaming and antipriming agents in steam generators. For application in certain foaming problems, these sulfonamides should possess certain limiting characteristics as regards molecular size as hereinafter more fully described.

Fundamentally speaking, the compounds involved in the practice of the present invention can be illustrated by the following structural formula:



in which X is the hydrocarbon radical of a sulfonic acid from the group consisting of aliphatic and aromatic sulfonic acids—i. e., $\text{X}-\text{SO}_2$ is the sulfonyl radical of an aliphatic or aromatic sulfonic acid; Y is the residue of an amine from the group consisting of the alkylene amines, including the alkylenediamines and polyalkylene polyamines, and the aromatic polyamines; and Z is a member of the group consisting of hydrogen, an acyl radical, and the sulfonyl radicals of aliphatic and aromatic sulfonic acids. Where Z is a sulfonyl radical, it may be identical with or different from the sulfonyl radical $\text{X}-\text{SO}_2$.

The sulfonamides which I have found to be most useful in reduction or elimination of foaming are the disulfonamides of long chain aliphatic sulfonic acids. For application in certain foaming problems, the hydrocarbon radical, i. e., X in the above probable structural formula, should contain at least about 12, and preferably 16 or more, carbon atoms, although for other purposes

compounds in which the radical X contains fewer carbon atoms may be satisfactory. Also of value are certain sulfonamides of dibasic sulfonic acids, such as decane 1,10-disulfonic acid.

The preparation of a number of suitable anti-foaming agents is described hereinbelow, and while the examples disclose some of the satisfactory preparative procedures, in most cases the same product may be obtained by more than one method.

The most-used method of preparation involved the use of a sulfonyl chloride with a nearly theoretical amount of an amine. In the preparation of the disulfonamides, two mols of the desired sulfonyl chloride were reacted with 1 mol of an amine which might be a polyalkylene polyamine, such as diethylene triamine, triethylene tetramine, tetraethylene pentamine, and analogous amines in which one or more of the alkylene groups are propylene, butylene, and higher alkylene groups, or an alkylene diamine in which the alkylene group might contain 1, 2, 3 or more carbon atoms, or an aromatic polyamine such as o-, m-, or p-phenylene diamine, benzidine, diamino-benzophenone, 4-amino-diphenylamine, diamino diphenyl ether, and other like amines. After mixing the selected sulfonyl chloride and amine, heat is applied to effect the desired reaction.

Unsymmetrical sulfonamides were prepared by reacting an amine, suitably a polyamine, with two different sulfonic acid chlorides or by other procedures.

Particularly efficient antifoaming agents falling within the scope of the present invention include the condensation products made from:

(1) cetyl sulfonyl chloride and diethylene-triamine;

(2) lauryl sulfonyl chloride with triethylene-tetramine;

(3) a sulfonyl chloride (formed by the reaction of a sulfonated long chain hydrocarbon, having 13 to 18 carbon atoms, the sodium salt of which is sold under the name of "M. P. 189" by E. I. du Pont de Nemours & Company, with PCl_5), and triethylenetetramine;

(4) the sulfonyl chloride prepared from "mahogany soap" (the sodium salt of the oil-soluble petroleum sludge sulfonic acids), and triethylene-tetramine;

(5) cetyl sulfonyl chloride and ethylenediamine;

(6) cetyl sulfonyl chloride and benzidine;

(7) cetyl sulfonyl chloride and hydroxy-ethyl-ethylenediamine;

(8) cetyl sulfonyl chloride and ammonium hydroxide and then formaldehyde;

(9) cetyl sulfonyl chloride and ethylene-diamine and subsequently acetyl chloride;

(10) cetyl sulfonyl chloride and hydrazine and subsequently dichloroacetone;

(11) cetyl sulfonyl chloride, diethylene-triamine, and benzene sulfonyl chloride;

(12) sulfonyl chloride prepared from a detergent composition known as General Aniline & Film Corp. "S. A. 151" (a sodium salt of a carboxylated sulfonic acid) and diethylenetriamine; and

(13) the reaction product of oleic acid with chlorosulfonic acid and subsequently with diethylene-triamine.

Other materials of value include the following: dilauryl sulfonamide of diethylenetriamine; dicetyl sulfonamide of triethylenetetramine;

dicetyl sulfonamide of 1,3-diamino-propanol-2;

dicetyl sulfonamide of o-phenylenediamine;

dicetyl sulfonamide of hydrazine;

dicetyl sulfonamide of propylenediamine;

monocetyl sulfonamide of acetyl diethylene-triamine;

dicetyl sulfonamide of methylenediamine;

reaction product of mono-oleyl ethylenediamine and the sulfonyl chloride of "S. A. 151";

reaction product of sulfonated oleic acid and diethylenetriamine.

The number of different compounds which can be prepared is quite numerous, and while a large number of examples are given hereinafter, it is to be understood that the invention is not to be limited to those specifically described, nor to the species to which the more limited are directed. The examples are as follows:

Example 1.—Cetyl sulfonic acid was neutralized to form a sodium salt and treated with PCl_5 to form cetyl sulfonyl chloride. 18.3 parts by weight of cetyl sulfonyl chloride so prepared was mixed with 3 parts by weight of diethylenetriamine and the mixture heated at 150 to 160° C. for three hours with stirring. The product so formed was a highly effective agent for retarding foaming in boilers.

By a similar procedure, dicetyl sulfonamides of triethylenetetramine, hydrazine, propylenediamine and 1,3-diamino-propanol-2 were prepared. These disulfonamides likewise were effective antifoaming agents.

Example 2.—6 parts of lauryl sulfonyl chloride were added to 1.9 parts of triethylenetetramine, and the mixture was heated at 150 to 160° C. and maintained at that temperature for two hours. The resulting product was an excellent antifoaming agent.

By the same procedure, the dilauryl sulfonamide of diethylenetriamine was obtained and found to be an antifoaming agent.

Example 3.—14 parts of a detergent material, presumably a sodium sulfonate, known as "du Pont's M. P. 189" was mixed with 10 parts of PCl_5 , and the mixture was heated under reflux at 150° C. for one hour. The mixture was then extracted with benzene, the extract dried over CaCl_2 and the benzene evaporated off. 2.2 parts of the residual sulfonyl chloride was reacted at a temperature of from 150 to 160° C. with 0.7 part of triethylenetetramine for a period of two hours to yield a reaction product effective as an antifoaming agent.

Example 4.—20 parts of "mahogany soap" was mixed with 50 parts of PCl_5 and heated under reflux at 150° C. for one hour. The reaction product was extracted with hot benzene and the benzene solution filtered. The extract was washed with cold water and the benzene layer dried over CaCl_2 , filtered and evaporated. To 16 parts of the residue was added 3 parts of triethylene-tetramine. The mixture was stirred and heated at 150 to 160° C. for three hours. The material obtained as a result of this reaction was an antifoaming material.

Example 5.—648 parts of cetyl sulfonyl chloride and 88.5 parts of ethylenediamine (68%) were heated at 150° C. for three hours. The reaction product was effective to reduce foaming in a steam boiler in which the water contained large quantities of dissolved solids.

Example 6.—648 parts of cetyl sulfonyl chloride and 184.1 parts of benzidine were mixed and

heated at 150 to 160° C. for three hours with occasional stirring. The product was effective as an antifoaming agent.

The dicetyl sulfonamide of o-phenylene diamine was prepared under the same reaction conditions and formed an effective antifoaming agent.

Example 7.—648 parts of cetyl sulfonyl chloride and 104 parts of hydroxy-ethyl-ethylenediamine were heated for three hours at 150 to 160° C. with occasional stirring. The reaction product was an effective antifoaming agent.

Example 8.—50 parts of cetyl sulfonyl chloride was mixed with a molecular excess of NH_4OH and the mixture was warmed to insure formation of cetyl sulfonamide. This sulfonamide was mixed with a molecular excess of formaldehyde and heated for two hours at 150 to 160° C. The resulting product was a highly effective antifoaming agent.

Example 9.—30 parts of cetyl sulfonyl chloride were mixed with a molecular excess of ethylenediamine, and the mixture was heated at 150 to 160° C. After an hour, a molecular excess of acetyl chloride was added, and heating was continued at the same temperature for an additional hour to insure complete reaction. The resulting product was a valuable antifoaming agent.

Example 10.—Molecular equivalents of hydrazine and cetyl sulfonyl chloride were mixed and heated with stirring at 150 to 160° C. for three hours. To the monocetyl sulfonyl hydrazine so formed, a molecular equivalent of dichloroacetone was added, and the mixture heated for 30 minutes at a temperature of 150° C. to effect a coupling reaction. The reaction product had antifoaming properties.

Example 11.—34 parts of diethylenetriamine were mixed with 108 parts of cetyl sulfonyl chloride and 59 parts of benzene sulfonyl chloride. The mixture was heated at 150 to 160° C. with stirring for three hours, and the reaction product produced was an antifoaming agent.

Example 12.—200 parts of the detergent compound known as "General Aniline & Film Corp. S. A. 151" was acidified with sulfonic acid and extracted with ether. The ether extract was washed and dried over CaCl_2 , and the ether was then evaporated. 30 parts of the acid so obtained were reacted with 8 parts of SOCl_2 in a vessel fitted with a reflux condenser, the SOCl_2 being added over a period of 23 minutes while the container was held at 80 to 90° C., and then held at this point for two hours under continuous stirring. The reflux condenser was then removed and the contents of the container stirred at 150° C. to drive off any excess SOCl_2 . 20 parts of the sulfonyl chloride so obtained was mixed with 2 parts of diethylenetriamine and the mixture heated with stirring at 150 to 160° C. for three hours. The reaction product was effective as an antifoaming agent.

Example 13.—5.5 parts of chlorosulfonic acid were added to 14 parts of oleic acid and the mixture was heated at 150 to 160° C. for 30 minutes. 6 parts of diethylenetriamine were then added and the mixture then heated at 150 to 160° C. for three hours, with stirring. The resulting composition was an effective antifoaming agent.

The products hereinabove described, while not ordinarily regarded as appreciably soluble in water, can be dispersed in water or emulsified therein by known methods so that effective amounts thereof can be introduced and be present in the water within the liquid to prevent foaming 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, for example, castor oil.

The amounts of these sulfonamides which are required are extremely small, and in general one grain per gallon is ample. For many purposes, however, amounts of as little as $\frac{1}{100}$ grain per gallon in the feed water introduced into a boiler will give valuable results. The amounts may be even further reduced; for example, where the feed water contains $\frac{1}{100}$ grain per gallon of a typical boiler water which contains solids which would cause foaming, foaming will be suppressed during evaporation of steam in the boiler for a period from 15 to 20 minutes. As contrasted with this, where castor oil is incorporated with feed water in amounts of the order of $\frac{1}{10}$ grain per gallon, the boiler will produce foam within 30 seconds to one minute. Accordingly, it is obvious that if one were to use castor oil, it would have to be injected into the boiler continuously, and there would unavoidably accumulate in the boiler quantities of soap produced by the reaction of the liberated fatty acids with the alkali present in the water, which would aggravate the tendency to foaming. The sulfonamide compounds of the present invention, however, are quite stable and do not yield undesirable by-products.

A comparison of the operation of castor oil with the operation of the material described above in Example 1 showed that while 380 parts per billion of castor oil in the feed water permitted a maximum increase of dissolved solids in the boiler water from 154 to 237 grains per gallon before development of foaming, a dosage of 128 parts per billion of the material of Example 1 permitted the dissolved solids in the boiler water to rise to 870 grains per gallon without excessive foaming, priming, or carry-over. Depending, of course, upon the degree of concentration of solids, the dosage may be varied, but one grain per gallon in the feed water is about as much as would ever have to be used even under serious conditions, and for many purposes $\frac{1}{100}$ grain per gallon, and even less, can be used. The process is particularly effective in the prevention of foaming at pressures of about 250 lbs. per square inch, as well as at pressures lower and higher. These materials are effective in boilers over a wide range of pressure up to and over 1000 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 antifoaming compounds into the feed water may be used, so that the introduction will be more or less in proportion to the steam output 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. While the

invention has been described in its use to prevent foaming in the steam boilers, it has been found also to be applicable to the general suppression of foaming in other liquids such as may be used in the production of sodium aluminate; paper manufacture to suppress foam in the beaters or in the machine, chests, etc.; and in the manufacture or utilization of adhesives, etc.

The invention therefore is not to be limited by the manner of introduction of the antifoaming composition or to the treatment of boiler water, but rather is to be construed in the terms of the hereunto appended claims.

I claim:

1. Process of minimizing the production of foam in and the priming of steam generators operating under superatmospheric pressures which comprises incorporating with a water therein containing an amount of total solids tending to produce foaming and priming, a quantity of a disulfonamide of a straight chain alkyl sulfonic acid containing more than 11 carbon atoms and a polyamine in sufficient amount to substantially inhibit priming and foaming, said sulfonamide not being appreciably soluble in water but capable of being dispersed in water and being substantially nonvolatile with steam.

2. Process of minimizing the production of foam in and the priming of steam generators operating under superatmospheric pressures which comprises incorporating with a water therein containing an amount of total solids tending to produce foaming and priming, a quantity of a dicetyl sulfonamide of diethylenetriamine sufficient to substantially inhibit priming and foaming.

3. Process of minimizing the production of foam in and the priming of steam generators operating under superatmospheric pressures which comprises incorporating with a water

therein containing an amount of total solids tending to produce foaming and priming, a quantity of a dilauryl sulfonamide of triethylenetetramine sufficient to substantially inhibit priming and foaming.

4. Process of minimizing the production of foam in and the priming of steam generators operating under superatmospheric pressures which comprises incorporating with a water therein containing an amount of total solids tending to produce foaming and priming, a quantity of a dicetyl sulfonamide of ethylenediamine sufficient to substantially inhibit priming and foaming.

5. A process of minimizing the production of foam in and the priming of steam generators operating under superatmospheric pressures which comprises incorporating with a water therein containing an amount of total solids tending to produce foaming and priming, a quantity of a disulfonamide of a straight chain alkyl sulfonic acid containing more than 11 carbon atoms and a polyalkylene polyamine in sufficient amount to substantially inhibit priming and foaming, said sulfonamide not being appreciably soluble in water but capable of being dispersed in water and being substantially non-volatile with steam.

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