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UNITED STATES PATENT OFFICE

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METHOD OF INHIBITING FOAM FORMATION IN STEAM GENERATION

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1 Claim. (Cl. 252—321)

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This invention relates to a method of conditioning water for the prevention or reduction of foaming.

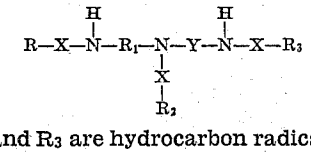
An object of the invention is to provide a method for the prevention or reduction of moisture entrainment in steam generating systems.

A further object of the present invention is to increase the coefficient of heat transfer in boilers, cooling equipment, heat exchange systems, and the like, without producing a foaming condition.

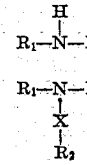
Foaming of boiler water is not, as is commonly thought, equivalent to an accumulation of foam on top of the surface of the boiler water. When steam is rapidly withdrawn from a boiler with resultant foaming, there is no water surface within the boiler correlated with the water level indicated in the conventional water glass attached to the boiler. In other words, there is no sharp line of demarcation between solid water and foam in the boiler during rapid steam withdrawal.

The foaming of boiler water is the result of steam being generated from numerous nuclei on the heating surface to produce myriads of permanent small bubbles which resist coalescence. Consequently, the entire volume of the water in the generating area is expanded by a mass of bubbles until the thus formed "light water" fills the steam space and becomes entrained with the steam leaving the boiler, thus producing a foaming condition.

I have now found that the foaming of boiler water can be substantially or completely inhibited by adding to a water having a tendency to foam on boiling, a compound having the general formula:



where R and R_3 are hydrocarbon radicals selected from the group consisting of alkyl, alkenyl, cycloalkyl and aralkyl radicals and substituted alkyl, alkenyl, cycloalkyl and aralkyl radicals containing at least 11 carbon atoms; X is a radical selected from the group consisting of carbonyl and sulfonyl radicals, at least one of the radicals represented by X being a sulfonyl radical; R_1 is an alkylene group; R_2 is a hydrocarbon radical, and Y is a grouping selected from the group consisting of R_1,



and

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and of combinations thereof. Preferably R and R_3 contain at least 11 or, better still, at least 15 carbon atoms. R, R_2 and R_3 may all be the same, but R_2 may also be a short chain hydrocarbon.

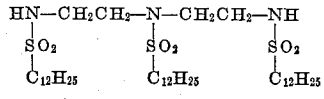
The compounds of the present invention contain at least one sulfonamide group, and preferably three to seven sulfonamide groups. If desired, a suitable foam-inhibiting compound may be prepared by first acylating a polyalkylene polyamine with a higher fatty acid to cause the formation of two or more amide groups on the nitrogen atoms of the polyalkylene polyamine, and thereafter reacting the polyamide thus produced with a high molecular weight sulfonyl chloride thus forming one or more sulfonamide groups on the nitrogen atoms which have not been acylated by the fatty acid.

Excellent foam inhibitors may also be prepared by first reacting a polyalkylene polyamine with a long chain sulfonyl chloride and reacting the product thus produced with a short chain sulfonyl chloride. It has been found that the primary amino groups of the polyalkylene polyamine are preferentially acylated in the initial reaction so that the short chain sulfonamide groups will be attached to the secondary amine groups in the molecule.

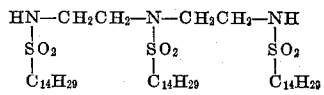
Examples of the previously mentioned types of compounds are listed below:

Compounds of the above general formula, where Y is CH_2CH_2.

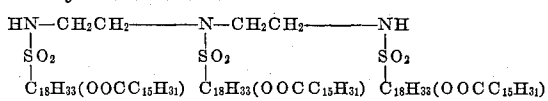
(1) Trilauryl sulfonamide of diethylene triamine—



(2) Trimyristyl sulfonamide of diethylene triamine—

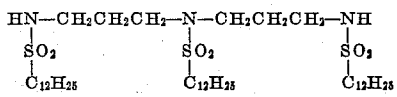


(3) Tri (palmitated ricinoleyl) sulfonamide of diethylene triamine——



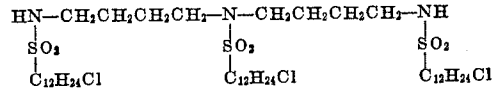
Compounds of the above general formula, where Y is $CH_2CH_2CH_2$.

(4) Trilauryl sulfonamide of dipropylene triamine—

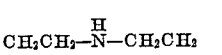


Compounds of the above general formula, where Y is $CH_2CH_2CH_2CH_2$.

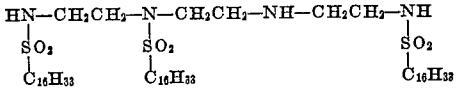
(5) Trichlorolauryl sulfonamide of dibutylene triamine—



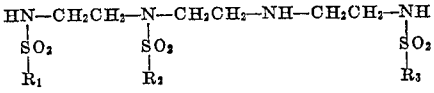
Compounds of the above general formula, where Y is



(6) Tricetyl sulfonamide of triethylene tetramine—

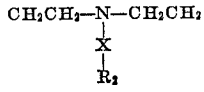


(7) Trinaphthenyl sulfonamide of triethylene tetramine—

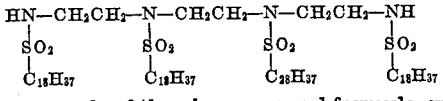


where R_1, R_2 and R_3 are each the residue of a naphthenic acid.

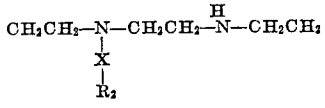
Compounds of the above general formula, where Y is



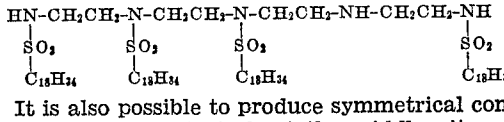
(8) Tetrastearyl sulfonamide of triethylene tetramine—



Compounds of the above general formula, where Y is

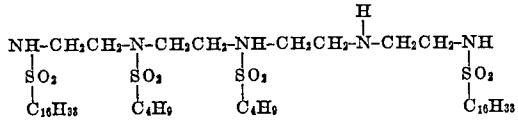


(9) Tetraoleyl sulfonamide of tetraethylene pentamine—

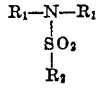


It is also possible to produce symmetrical compounds (symmetrical about the middle nitrogen atom) by the syntheses disclosed in this specification.

(10) Dicethyl dibutyl sulfonamide of tetraethylene pentamine—

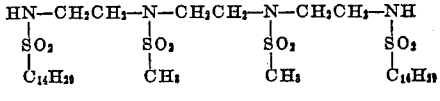


Compounds of the above general formula, where Y is

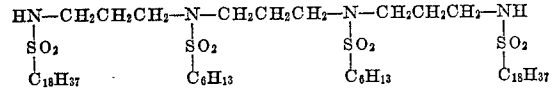


and R_2 are short chain alkyl groups.

(11) Dimyristyl dimethyl sulfonamide of triethylene tetramine—

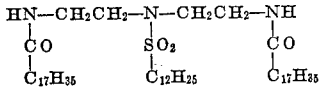


(12) Distearyl dihexyl sulfonamide of tripropylene tetramine—

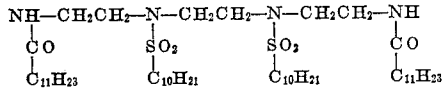


Examples of mixed amide-sulfonamide compounds are as follows:

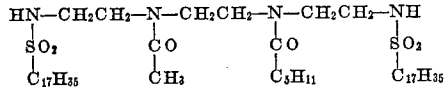
(13) Distearamide monolauryl sulfonamide of diethylene triamine—



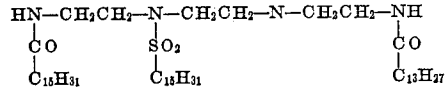
(14) Dilauramide didecylsulfonamide of triethylene tetramine—



(15) Distearylsulfonamide capro-acetamide of triethylene tetramine—



(16) Palmityl sulfonamide palmitoyl myristylamide of triethylene tetramine—



While the above exemplary formulae generally indicate that the hydrocarbon substituents of the terminal amide or sulfonamide groups are identical, it will be appreciated that the material used in preparing these compounds will normally be commercial reagents, such as coconut oil fatty acids, soybean oil and the like, which contain mixtures of acids of varying chain length and hydrogen content. Thus R and R_3 given in the general formula could easily be different hydrocarbon radicals.

The preparation of the compounds listed above can be accomplished through a variety of means. In general, the sulfonamides may be prepared by reacting one molecular proportion of a polyalkylene polyamine with three or more molecular proportions of an alkyl sulfonyl chloride. The reaction conditions will vary with the compounds used, but in general the condensation may be effected by simply mixing the ingredients together in the appropriate proportions, and heating to a temperature in the range from about 100 to 250° C., normally between 180 and 220° C. The individual reaction products need not be separated from the reaction mixture, but the mixture as a whole may be used as a foam inhibitor.

Suitable polyalkylene polyamines are of the type of diethylene triamine, triethylene tetramine, tetraethylene pentamine, dipropylene triamine, tripropylene tetramine, dibutylene triamine, tributylene tetramine, and the like.

The long chain sulfonamide groups may be attached by reacting a polyalkylene polyamine of the type mentioned above with a long chain alkyl, naphthenyl, aryl or aralkyl sulfonyl chloride such as, for example, lauryl sulfonyl chloride, cetyl sulfonyl chloride, myristyl sulfonyl chloride, oleyl sulfonyl chloride, stearyl sulfonyl chloride, naphthenyl sulfonyl chloride, dodecyl benzene sulfonyl chloride, and the like. The sulfonated derivatives of the naphthenic acids obtained from petroleum are available commercially as the

"green acids" and the "mahogany acids" and may be used in the preparation of the naphthenyl sulfonyl chlorides. The aralkyl sulfonates prepared by alkylating benzene or toluene with a propylene tetramer are also readily available. These sulfonated products may be easily converted into the sulfonyl chlorides by reaction with agents such as phosphorus pentachloride. Another method for preparing the sulfonyl chloride involves condensing the appropriate alkyl halide with a bisulfite such as sodium bisulfite.

When it is desired to introduce a shorter chain into the compounds to aid in dispersing the same in water, the polyalkylene polyamine is first reacted with two or more moles of the long chain sulfonyl chloride, and subsequently with a relatively short chain alkyl sulfonyl chloride. Typical of the latter compounds are methyl sulfonyl chloride, butyl sulfonyl chloride, hexyl sulfonyl chloride, and decyl sulfonyl chloride. In general, the short chain compounds should contain between one and ten carbon atoms.

Where a mixed amine sulfonamide type foam inhibitor is to be prepared, the polyalkylene polyamine is first acylated with a fatty acid containing eleven or more carbon atoms in its hydrocarbon chain. This step may be carried out by heating the fatty acid with the polyalkylene polyamine in molecular ratios of 2 parts or more of acid to one part of polyamine at a temperature in the range of about 150° to about 200° C. The acylated product is then reacted with a sulfonyl chloride as previously described. The procedure may also be reversed, in that the polyalkylene polyamine may be reacted with the sulfonyl compound in the first instance to form the sulfonyl groups on the terminal nitrogen atoms, and this product may be subsequently acylated with a long or short chain fatty acid.

The various hydrocarbon chains in the molecules may contain other constituents, such as hydroxy, ester, ether, halide, or thio groups. For example, a substituted ricinoleyl sulfonyl chloride makes an excellent starting material for the preparation of the sulfonamides of the present invention.

The preferred compounds of the present invention are those resulting from the condensation of one molecular proportion of a polyalkylene polyamine with three or more molecular proportions of a high molecular weight sulfonyl chloride preferably containing at least eleven and preferably fifteen carbon atoms in the hydrocarbon chain attached to the sulfonyl group. A typical compound of this type is the trilauryl sulfonamide of diethylene triamine. This may be prepared from lauryl alcohol and diethylene triamine as follows: Lauryl alcohol is first sulfonated with sulfuric acid, oleum or other sulfonating agent to produce a lauryl sulfonic acid. The sulfonic acid is next reacted with a chlorinating agent such as phosphorus pentachloride, or thionyl chloride, or the like to produce the lauryl sulfonyl chloride. Three or more molecular proportions of the sulfonyl chloride are then reacted with one molecular proportion of diethylene triamine by heating the two reactants together at a temperature in the range from about 180 to 220° C. The reaction products may be used without separation of the individual constituents and the product functions as a very efficient foam inhibitor.

The foam inhibiting compositions of the present invention may be introduced into the steam boiler water in the form of colloidal dispersions that may be stabilized with tannin, gum arabic, pectin, or the like. The foam inhibiting compounds may be incorporated into a powdered formula containing tannin, soda ash, and metallic activators such as lanthanum chloride. If desired, the foam inhibiting compositions may be introduced into the boiler in the form of a solution in an appropriate solvent, such as isopropyl alcohol or the like. When a powdered formula is used, this formula may be added manually directly to the locomotive tender, or the powder may be dissolved in water in mixing vats and subsequently pumped into the feed water storage tanks in specific proportions with the feed water to obtain uniform treatment of the water. Addition of foam inhibiting compounds may be repeated as required to prevent foaming.

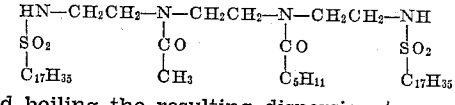
The dosages required are generally quite small, on the order of a few parts per million of boiler water. In addition, from about 0.1 to about 50 parts per million of the active foam inhibiting compounds may be added to the boiler water, preferably in combination with tannin.

While compositions of the type disclosed herein are primarily for use in inhibiting foam formation in waters or aqueous media boiled at superatmospheric pressures, they may also be used in steam boilers and the like operated at atmospheric and sub-atmospheric pressures.

Various details of the invention herein disclosed may be varied through a wide range without departing from the principles of this invention, and it is not my purpose to limit the patent granted on this invention otherwise than necessitated by the scope of the appended claim.

I claim as my invention:

The method of inhibiting foam formation in water having a tendency to foam on boiling which comprises dispersing into said water in an amount sufficient substantially to inhibit said tendency, a compound having the formula



and boiling the resulting dispersion to generate steam therefrom.

LEWIS O. GUNDERSON.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,449,656	Kell	Sept. 21, 1948