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UNITED STATES PATENT OFFICE

2,647,088

METHOD OF INHIBITING FOAMING IN WATER

Lewis O. Gunderson, Park Ridge, Ill., assignor to Dearborn Chemical Company, Chicago, Ill., a corporation of Illinois

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7 Claims. (Cl. 252—321)

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This invention relates to a method of conditioning water for the prevention of foaming. The invention further pertains to compositions of matter adapted for use in the conditioning of water for steam boilers and to methods for preparing such compositions.

The compositions in general may be characterized as acylated alkylene polyamine imidazolines, or substituted imidazolines.

This application is a continuation-in-part of my copending application entitled "Method of Conditioning Water," Serial No. 501,293, filed September 4, 1943.

Foaming of boiler water is not, as commonly thought, equivalent to an accumulation of foam on top of the surface of the boiler water. When steam is rapidly withdrawn from the boiler with resultant foaming, there is no water surface within the boiler correlated with the water level indicated in the conventional waterglass 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 coalescense. 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 more or less spontaneous formation of vast numbers of small steam bubbles that result in expansion of the water volume to a point where it substantially fills the boiler and is entrained with the steam withdrawn may be largely or completely inhibited by the addition to the boiler water of compositions containing, as active ingredients, condensation products of high molecular weight carboxylic acids with imidazolines of aryl diamines, alkylene diamines, polyalkylene polyamines, and hydroxy polyalkylene polyamines. The higher fatty acids, containing twelve or more carbon atoms per molecule, are especially well suited as acylating agents. Typical among these higher fatty acids are lauric, stearic, oleic, palmitic, ricinoleic, linoleic, myristic acids, and the like.

An object of the present invention is to provide a method of conditioning water used in steam generating to minimize the entrainment of water with the steam leaving the boiler.

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A further object of the present invention is to provide an efficient method for generating steam from boiler water having a tendency to foam on boiling.

A further object of the present invention is to provide compositions for use in conditioning boiler water.

Other and further objects of the invention will become apparent to those skilled in the art from the following description and appended claims.

I have found that foam formation of boiler water may be inhibited by incorporating into the water in an amount sufficient substantially to inhibit the tendency to foam on boiling, an imidazoline compound prepared by reacting a polyamine with a carboxylic acid compound to form an imidazoline, and acylating the imidazoline thus produced with a high molecular weight carboxylic acid. The compounds used according to the present invention to prevent foam formation are, in general, surface-active and predominantly hydrophobic.

The specific organic compounds to which the present invention particularly relates comprise high molecular weight acylation products of the imidazolines of the aryl poly amines such as diphenylene diamine, the alkylene diamines such as ethylene diamine and hexamethylene diamine, the polyalkylene polyamines such as diethylene triamine, triethylene tetramine, tetraethylene pentamine, dipropylene triamine and tripropylene tetramine, and the like. The carboxylic acids used for acylating purposes may be substituted or unsubstituted, straight chain or branched, saturated or unsaturated. In addition to the conventional fatty acids, other acids such as those obtained from petroleum products or by organic synthesis may be used. Of special utility in the connection are the naphthenic acids recoverable in the refining of petroleum. These acids have been characterized as having a cyclopentane structure with long alkyl chains attached thereto, and usually contain one carboxyl group per molecule. The naphthenic acids have in general more than twelve carbon atoms per molecule and a neutralization equivalent in the range from about 225 to about 400. In using the naphthenic acids in accordance with the present invention, I prefer to use those acids which have neutralization equivalents between 250 to 320.

Acylation of the polyalkylene polyamines incidental to the preparation of the imidazolines may also be carried out by condensing the poly-

alkylene polyamines with a fatty glyceride, for example, tallow, coconut oil, lard oil, cottonseed oil, peanut oil, soybean oil, castor oil, whale oil, sardine oil, tall oil, and the like, which contain predominately acyl groups having 18 carbon atoms, and some having as many as 20 carbon atoms.

The initial production of the imidazoline may be accomplished by using a carboxylic acid compound of any desired chain length. Thus, short chain acids such as acetic, butyric, caproic, and capric acid may be used as well as the preferred long chain acids.

In addition, dibasic acids, such as sebacic acid, succinic acid, and adipic acid, may be condensed with the polyamines to form compounds having two imidazoline rings separated by a hydrocarbon chain.

The polyalkylene polyamine and the carboxyl-containing compounds are reacted together at temperatures of approximately 250° to 300° C., with agitation, until the reaction product is soluble in water, indicating imidazoline formation. The imidazoline product may be crystallized from the reaction mixture and subsequently acylated with the fatty acids and the like to form the acyl derivatives of the imidazoline. If desired, the acylation reaction may be carried out on the reaction product without intermediate separation, in which case the subsequent acylation steps will yield a mixture of acylated imidazoline derivatives and acyl derivatives of the polyalkylene polyamines.

After the acylation reaction has been carried out, there may remain a residual unreacted organic acid content or partial glyceride content, which, however, need not be removed from the high molecular weight imidazoline polyamide compound but may be retained in the final product. These residual fatty acids or fatty acid derivatives, such as esters and partial glycerides, have proven in certain instances to be beneficial in the process of foam prevention, being helpful in dispersing the active ingredients when added to the boiler feed water and also cooperating in conditioning the boiler water to prevent foam formation and, in particular, to prevent the phenomenon called "effervescence." By "effervescence" is meant the projection of small droplets of water into the steam space by the surfacing and rupture of tiny gas or vapor bubbles originating in the body of water whereby a considerable proportion of such droplets become entrained with the steam leaving the boiler. Effervescence seems to be correlated with the amount of dissolved gases in the feed water and/or the presence of alkali and alkaline earth bi-carbonates therein, causing a dispersion of fine bubbles in the hot boiler water as the feed water is injected into the boiler. Entrainment of the projected particles of water is accentuated by an increase of surface tension and an increase in hydration of steam bubble films. This effervescence phenomenon may be inhibited without interfering with the foam prevention in the boiler by adding to the foam inhibiting composition a surface tension reducing substance in the form of soluble fatty acid soap, resin acid soap, and high molecular weight wetting agents, for example, a sulfonated lauryl alcohol such as "Duponol."

The reaction products obtained from the processes disclosed herein are mixtures of compounds difficult to separate, identify, or characterize, but are thought to comprise acylated imidazolines, acylated amines, and complexes thereof, and other cyclic compounds.

The effectiveness of the foam inhibitors was determined in a laboratory boiler operating at 200 pounds per square inch pressure and containing 1000 cc. of a foaming water made up by adding one-half gram of $CaSO_4.2H_2O$, two grams anhydrous Na_2CO_3, and three grams anhydrous Na_2SO_4 to one liter of distilled water. One milligram of the anti-foam compound to be tested was dissolved in alcohol and flushed into the boiler. The effectiveness of the compound was measured by the length of time foaming was inhibited while steam was withdrawn at intervals from the boiler.

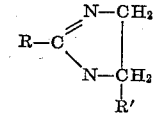
Examples of the compounds which may be used in accordance with the present invention are as follows.

In the following exemplary formulae:

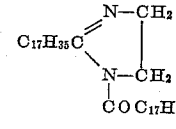
R is a carboxylic acid residue of any chain length;
R′ is COR or $(C_2H_4NR'')_m—C_2H_4—NHCOR$;
R″ is H or COR;
R‴ is COR;
m is 0 or a whole number less than 15; and
n is a whole number greater than 1 and less than 15.

In any event, the acyl groups shown above and in the following formulae should contain a total of at least 12 carbon atoms. Where the "R" substituent in the number two position in the imidazoline ring has less than about 12 carbon atoms, the acyl groups should contain at least 16 carbon atoms, and preferably 18 carbon atoms.

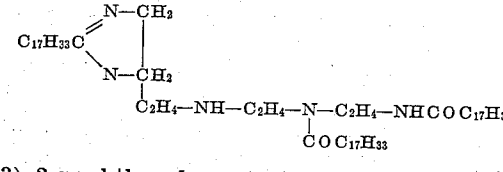
A. Acylation product of a mono-imidazoline.



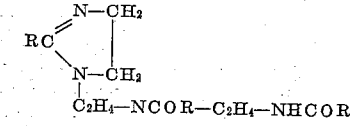
(1) 1-stearoyl, -2-stearyl imidazoline.



(2) 2-oleyl, -1-di-oleoyl-triethylenetriamino-imidazoline.

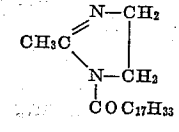


(3) 2-naphthenyl, -1-dinaphthenoyl-di-ethyl-enediamine-imidazoline.

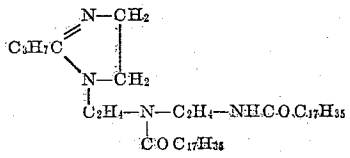


where R is a naphthenic acid residue.

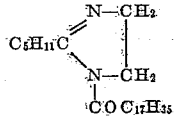
(4) 2-methyl, -1-oleoyl imidazoline.



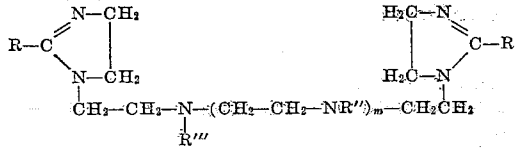
(5) 2-propyl, -1-distearoyl-diethylenediamino imidazoline.



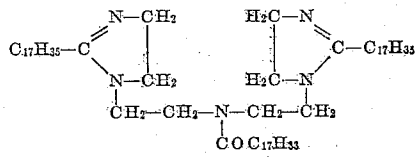
(6) 2-amyl, -1-stearoyl imidazoline.



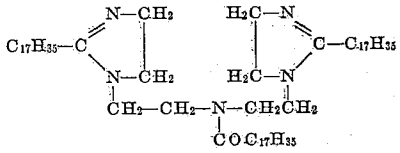
B. Acylation product of compounds having two imidazoline rings.



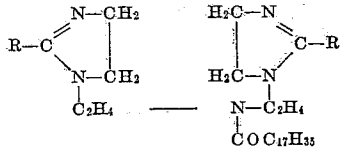
(1) N-oleoyl,di-2-stearylimidazoline of tetraethylenepentamine.



(2) N-stearoyl,di-2-stearylimidazoline of tetraethylenepentamine.

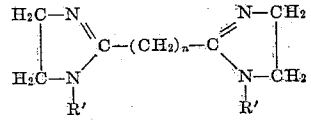


(3) N-stearoyl,-di-2-naphthenyl imidazoline tetraethylene pentamine.

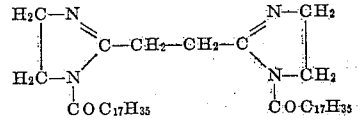


where R is a naphthenic acid residue.

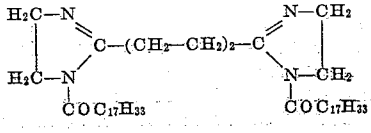
C. Acylation product of dibasic acids reacted with polyamines.



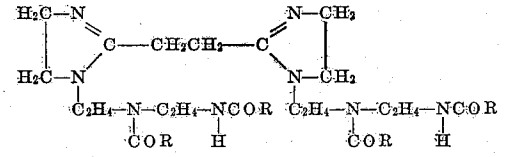
(1) Di-1-stearoyl imidazoline dimethylene.



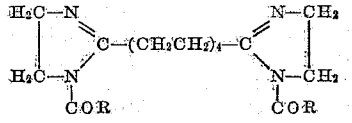
(2) Di-1-oleoylimidazoline tetramethylene.



(3) Di-1-di-naphthenoyl diethylene diamino imidazoline dimethylene.



(4) Di-1-naphthenoyl imidazoline octamethylene.



where R is a naphthenic acid residue.

Such compounds may be prepared in the manner described below:

Example I.—1-stearoyl, 2-stearyl imidazoline

2-stearyl imidazoline may be prepared from 55.6 grams of stearic acid (Armour "Neo-Fat" 1—60), 19.6 grams ethylenediamine hydrochloride and 9.0 grams of anhydrous ethylenediamine. The ethylenediamine hydrochloride and the stearic acid are throughly mixed in a 500 ml. round bottomed flask. The ethylenediamine is added slowly with agitation and the reaction mixture heated slowly to 100° C. under a reflux condenser attached to the side arm water separator. The temperature of the reaction mixture is raised slowly to 185° C. over a period of 90 minutes. A small amount of vapor begins to come over at 160° C. Between 160 and 185° C., 0.7 ml. of distillate are collected. The temperature is then raised to 250° C. over a period of 30 minutes, 2.4 ml. of distillate being collected during this interval. The temperature is raised rapidly (15 minutes) to 290° C., 3.8 ml. of distillate being collected. After further heating for 15 minutes, the product is soluble in water, giving a clear solution. The reaction mixture is dissolved in water and dilute sodium hydroxide added until no more crystals appear. The crystals of stearyl imidazoline are collected and dried in air. The product so obtained is then condensed, mole for mole, with stearoyl chloride to acylate the free amino group present.

For this purpose, the imidazoline is placed in a 200 ml. round bottomed flask and an equal weight of stearoyl chloride added slowly while agitating. Heat is evolved in the reaction. The reaction mixture is heated slowly to 100° C. Foaming occurs with the rapid evolution of hydrochloric acid. When the foaming subsides (10 to 15 minutes), the reaction mixture is heated to 160–185° C. with stirring and the temperature maintained until the evolution of hydrochloric acid ceases (approximately 4½ hours). The reaction product is twice recrystallized from benzene and acetone. The amide thus obtained (1-stearoyl, 2-stearyl imidazoline) melts at 80° to 90° C. and is soluble in benzene, alcohol and xylene, but is insoluble in acetone.

Example II.—2-stearyl, 1-oleoyl amino ethylene imidazoline (i. e., oleic acid amide of 2-stearyl, 1-amino-ethylene imidazoline)

This is made in like manner as the preceding compound excepting that oleic acid is substituted for stearoyl chloride in the second step and diethylenetriamine is substituted for ethylenediamine.

Example III.—Di-1-oleoyl imidazoline tetramethylene

44 grams adipic acid, 36 grams of ethylenediamine hydrate, and 44 grams of ethylenediamine hydrochloride are gradually heated in a fractionating flask having a capacity of 300 cc. and provided with a thermometer reaching into the bottom. At about 135° C. the hydrochloride dissolves in the liquid formed. The water and the excess of ethylenediamine hydrate distill, with slight foaming. The temperature is then raised, within half an hour, to about 225° C. and this temperature is maintained for about 15 minutes. It is thereupon raised, within half an hour, to 280° C. The melt, which is light yellow, begins to darken. The reaction mixture is maintained at 290–295° C. for an additional 5–10 minutes.

The dark colored melt, while hot, is stirred with about 160 grams of hot alcohol (95%) and boiled for half an hour, under reflux, until all the matter soluble in alcohol has dissolved; it is then filtered while hot, and the residue thoroughly washed two or three times, with 16 cc. of hot alcohol each time. The residue (9.5 gms.) which is insoluble in alcohol, consists for most part of ethylenediamine hydrochloride. The combined filtrates are treated with decolorizing carbon, filtered and concentrated to about 120 grams. On cooling, the whole solidifies to a crystalline mass, which is carefully filtered with suction and washed with three or four 10 cc. portions of alcohol. About 38 grams of a crystalline material moist with alcohol, probably di-imidazoline hydrochloride tetramethylene, are thus obtained.

Five grams of the di-imidazoline hydrochloride tetramethylene are dissolved with heating in 200 grams of absolute alcohol and allowed to cool completely. A solution of alcoholic KOH is slowly added, in the cold, to the solution of the di-imidazoline hydrochloride in absolute alcohol to just neutralize the hydrochloride. The KCl is precipitated. The whole is allowed to stand overnight and then filtered. The alcohol is then evaporated under reduced pressure. The yellow-white residue of di-imidazoline tetramethylene obtained is then acylated with oleic acid or oleoyl chloride in mole ratio of 1:2 similarly to the method employed in the previous example to form the di-1-oleoyl imidazoline tetramethylene.

Example IV

Di-1-stearoyl imidazoline dimethylene is made in the manner shown in Example III, except succinic acid is substituted for the adipic acid, and stearic acid for oleic acid. Di-1-naphthenoyl imidazoline octamethylene is made similarly, using sebacic acid and naphthenic acid.

Example V

Di-1-dinaphthenoyldiethylenediamine imidazoline dimethylene may be prepared as shown in Example III, except that 1 mole of succinic acid is condensed with 2 moles of triethylene tetramine to form the di-imidazoline which is further condensed with 4 moles of a naphthenic acid having a neutralization equivalent of about 300.

Example VI

An effective anti-foam was prepared utilizing different types of high molecular weight carboxylic acids, e. g., triethylene tetramine was reacted mole for mole with naphthenic acid having a neutralization equivalent of 300 by heating the compounds together for 6 hours at 250–275° C. until the reaction product became water soluble. The reaction product comprising imidazoline thus formed was then condensed with two moles of oleic acid to admidize the product. The crude reaction product probably comprised the compound 2,naphthenyl,1,di-oleoyl triethylene triamino imidazoline, as well as some polynaphthenoyl, polyoleoyl amides of triethylene tetramine and other complex cyclic compounds of unknown character.

The above-described methods of preparation are given to illustrate laboratory technique to obtain relatively pure imidazoline amide products for identification and characterization, but commercially satisfactory products have been made without attempting to separate and purify the desired end product. The crude reaction mixture has been found to be a practical and effective antifoam.

Example VII

One mole of myristic acid was condensed with 1 mole of diethylene triamine hydrochloride and 1 mole of diethylene triamine base, whereby the myristic acid and the amine hydrochloride were first mixed in the reactor and then slowly heated to 185° C. while the diethylene triamine base was added over a period of 2 hours. Then the temperature was increased to 250° C. in 30 minutes and to 290° C. in another 15 minutes, and kept at that temperature for another 30 minutes, after which the product was soluble in water, indicating the formation of the imidazoline.

The excess polyamine was then distilled off under vacuum, and the product was then further condensed with stearic acid at 185° C. ± 10° C. for 6 hours to produce the 2-myristyl, 1-stearoyl imidazoline amide (i. e. stearic acid amide of 2-myristyl, 1-aminoethylene imidazoline). It was an effective foam inhibitor of boiler water.

Also, the method of Hill and Aspinall, J. A. C. S., vol. 61, 822 (1939), produces a suitable starting product by reacting ethylene diamine and palmitic acid mole for mole for 4 hours at 290° C. or until the reaction product is water soluble. Thereupon the excess amine is vacuum distilled and the product further condensed with palmitic acid at 185° C. ± 5° C. for 4 hours to produce a water insoluble imidazoline amide, a good foam inhibitor.

Example VIII

One mole of naphthenic acid (neutral equivalent 310) and 2 moles of triethylene tetramine were condensed together at a temperature of 290° C. ± 10° C. for two hours, after which the excess amine was removed by vacuum distillation. The remaining water-soluble imidazoline was then further condensed with 2 moles of the naphthenic acid (neutral equivalent of 325) for 6 hours to produce a water-insoluble crude reaction product that was an excellent foam inhibitor of boiler water. The reaction product is probably a mixture of amides of the 2-naphthenyl-1-diethylene diamine imidazoline.

The following examples illustrate the production of naphthenoyl amides of imidazoline in crude reaction products:

Example IX

43 grams of 70% aqueous ethylene diamine (0.5 mole) and 161 grams of naphthenic acid having an acid number of 174.3 and a neutralization equivalent of 322 were condensed at a temperature of 100° C. for a period of 90 minutes, fol-

lowed by raising the temperature to 180° C. within 30 minutes, and thereupon raising the temperature to 290° C. and maintaining the latter temperature for a period of 30 minutes. The reaction product became soluble in water, indicating imidazoline formation. The reaction product was dissolved in water and diluted sodium hydroxide was added until no more crystals appeared. The crystals were then collected and dried in air. The product so obtained was condensed mole for mole with a naphthenic acid having a neutralization equivalent of 320 to acylate the free amino group by heating the reactants at a temperature of 185° C. for a period of 4½ hours. This reaction product showed excellent foam inhibiting effectiveness when tested in the experimental boiler.

Example X

One molecular proportion of tetraethylene pentamine was condensed with an equimolar proportion of a naphthenic acid having a neutralization equivalent of 230 by heating the mixture to a temperature of 275° C. until the reaction product became water soluble, indicating imidazoline formation. The reaction product was further condensed with 3 molecular proportions of a naphthenic acid having a neutralization equivalent of 250 at a temperature of 185° to 200° C. for 6 hours until the acid number remained substantially constant.

The reaction product was an effective foam inhibitor when tested in the laboratory high-pressure boiler.

Example XI

One molecular proportion of tetraethylene pentamine was condensed with two molecular proportions of a naphthenic acid having a neutralization equivalent of 250 at a temperature of 250° C. for 8 hours. The water-soluble reaction product was then acylated with another molecular proportion of the naphthenic acid at a temperature of 200° C. for 6 more hours.

The reaction product was found to be an effective foam inhibitor when used in the high-pressure boiler.

Similarly, triethylene tetramine may be reacted mole for mole with a naphthenic acid to form an imidazoline which is then condensed with 2 moles of a high molecular weight naphthenic acid to produce a compound which is probably 2,naphthenyl,1,di-naphthenoyl triethylene triamino imidazoline. This compound also showed excellent foam inhibiting properties.

The above represented compounds indicate various classes of acylated imidazolines that can be utilized in preparing foam inhibiting compounds. It will be understood that heterogeneous atoms may separate the imidazoline groups.

Other acylated imidazoline compounds having foam inhibiting properties can be prepared with various combinations of polar groups, with the inclusion of heterogeneous atoms in molecular structure, but the possible number of such combinations is so great that it would serve no purpose to list examples of all the various possibilities. The primary essential feature in the molecular structure of such compounds is that it contains several separated polar groups to which are attached high molecular weight hydrocarbon chains.

The above-described acylated derivatives of the imidazolines of ethylene diamine and higher polyalkylene polyamines illustrate the use for foam inhibiting purposes of compounds including spaced amide groups interconnected by carbon chains or chains containing both nitrogen and carbon, or any bivalent heterogeneous atom or radical.

The various foam inhibiting polyamides and imidazolineamides may be introduced into the boiler feed water or into the boiler water in a water-miscible organic solvent or in an emulsion that is miscible with the foaming water or solution.

The foam inhibiting compounds may be mixed with tannin or other emulsifying agent in a powdered formula comprising other synergistic and/or inert ingredients, including lignin derivatives, soda ash, sodium bicarbonate, and the like. The powdered formula may be added directly to the boiler feed water, or the boiler water, or a preliminary solution may be prepared that is subsequently added proportionately to the boiler feed water.

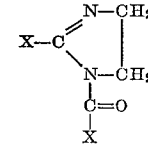
In general, a small amount of active foam inhibitor, from about one-quarter to fifty parts per million of the active compound will suffice to completely or substantially inhibit the foaming characteristics of a boiler feed water.

While the invention has been described with particular reference to boilers operating under superatmospheric pressures, the compounds of the present invention are also useful for inhibiting foaming at atmospheric or sub-atmospheric pressures. For example, the compounds herein disclosed are useful in inhibiting foaming in paper-making stocks, and in applications in the textile industry.

It will, of course, be understood that various details of the process may be varied through a wide range without departing from the principles of this invention, and it is, therefore, not the purpose to limit the patent granted hereon otherwise than necessitated by the scope of the appended claims.

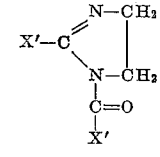
I claim as my invention:

1. 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:



wherein X is a non-aromatic hydrocarbon radical having 11–19 carbon atoms, and boiling the resulting dispersion to generate steam therefrom.

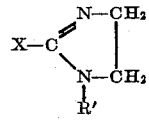
2. The method of inhibiting foam formation in water having a tendency to foam on boiling which comprises dispersing into said water in an amount sufficient substantially to inhibit said tendency, a compound having the formula:



wherein X′ is the hydrocarbon residue of naphthenic acid having the formula X′—COOH, and boiling the resulting dispersion to generate steam therefrom.

3. 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:



wherein X is a non-aromatic hydrocarbon radical having 11–19 carbon atoms; and R′ is a radical selected from the group consisting of —CO—X and —(C_2H_4—NR″)$_m$—C_2H_4—NHCO—X wherein R″ is a radical selected from the group consisting of —H and —CO—X; and m is an integer from 0 to 15, and boiling the resulting dispersion to generate steam therefrom.

4. A method as claimed in claim 3 wherein said compound is 1-stearoyl, 2-stearyl imidazoline.

5. A method as claimed in claim 3 wherein said compound is oleic acid amide of 2-stearyl, 1-aminoethylene imidazoline.

6. A method as claimed in claim 3 wherein said compound is stearic acid amide of 2-myristyl, 1-aminoethylene imidazoline.

7. A method as claimed in claim 3 wherein said compound is napthenic acid amide of 2-naphthenyl-1-diethylene diamine imidazoline.

LEWIS O. GUNDERSON.

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