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RALPH E. HALL, OF PITTSBURGH, PENNSYLVANIA, ASSIGNOR TO JOHN M. HOPWOOD,
OF DORMONT BOROUGH, PENNSYLVANIA

TREATMENT OF STEAM-BOILER WATER

No Drawing.

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This invention relates to the treatment of steam boiler water, and more particularly to its treatment for the prevention of foaming. Foaming is a condition encountered in boilers, particularly where the water contains soluble salts or saponifiable material, and consists in the formation of fine bubbles or foam in the steam space of the boiler. If a sufficient foam is formed, it is carried as entrained moisture through the steam outlet. This entrained moisture is highly objectionable in the steam-utilizing devices, such as steam engines and turbines, and is also very objectionable in its action in a superheater.

When steam is generated in a closed vessel, as a steam boiler, its delivery from the steam outlet devoid of droplets of boiler water and concomitant sludge, is a function among other things of the characteristics of the films of the liquid phase enveloping the individual steam bubbles, and the rate at which steam is delivered from the steam outlet. Thus, if the films enveloping the bubbles initially at the evaporating surfaces coalesce readily to form larger bubbles and these bubbles burst instantaneously at the steam-water interface of the steam drum, no layer of foam can be in existence more than momentarily, and any tiny droplets of boiler water, originating in the disruption of the film will be at a maximum distance from the steam outlet, and hence with minimum chance of being carried into the steam nozzle. But if the films do not burst instantaneously, then the steam bubbles are pushed higher in the steam space by the ensuing bubbles, and the final disruption of the film may occur at any elevation in the steam space, or even be so delayed that steam bubbles as such may enter the steam outlet from the boiler. Also, if a boiler is operating at low per cent of rating, it may deliver dry steam, whereas at high per cent of rating the steam may be seriously contaminated by entrained moisture. This follows because at low per cent of rating, the available time for the disruption of the steam bubble at a point in the steam space where it will be harmless is greater. Also, since the carrying power of a gas (steam) increases very rapidly with increase of velocity, at the high-

er per cent of rating, the steam will carry with it droplets of larger size, and therefore a larger fraction of all droplets formed, and thus increase the amount of entrained moisture in the steam.

In order to insure the minimum of entrained moisture in the steam at the steam outlet, therefore, it is necessary that the films of liquid phase enveloping the individual bubbles of steam should readily coalesce; that their duration should be as nearly nil as possible at the steam-water interface in the steam drum; and that any droplets formed in the bursting of the film should have the largest possible size.

The factors which influence the readiness of coalescence or disruption of the liquid-phase films enveloping the steam bubbles have been variously described. The contamination of the boiler water by oil has frequently been blamed for foaming. Likewise, foaming has been ascribed to a condition of carbonate or caustic alkalinity in the boiler water, to the sodium sulfate and sodium chloride therein, to the presence of suspended matter, and to the combined effect of suspended and dissolved solids.

In an extensive series of experiments conducted in experimental boilers in my laboratory, I have found that as successive additions of sodium sulphate, chloride, hydroxide, carbonate, or phosphate are made to distilled water in these boilers, the rate of coalescence and disruption of the liquid films enveloping the bubbles at the evaporating surfaces and the steam-water interface respectively steadily decreases, and the head of foam just as surely increases. For all of these materials, the specific effect under consideration was the same, but the amount of sulfate, chloride, etc. expressed in parts per million necessary to produce a like effect, was different. Also, the presence of a slight amount of iron hydroxide such as might be caused by corrosion of the iron or steel of the boiler, or the presence of other precipitates of similar character lessened the concentration of sulfate, chloride, etc. necessary to cause any chosen decrease in rate of film coalescence or disruption. Greater amounts of precipitates

of this type exercised a somewhat greater influence than the small amounts just described. The effect of oils was found to be closely connected with their composition and the caustic alkalinity of the boiler water. Thus, an oil, heavily compounded with a fatty material, in an alkaline water, produced a far greater effect than one less heavily compounded, because of the saponification by the alkali in the boiler water of the fats or other saponifiable material used on compounding the oil, and the consequent introduction in solution into the boiler water of soap with its well-recognized property of stabilizing liquid films against disruption.

Practically all natural waters are contaminated among other things with sodium sulfate and sodium chloride. Some waters also contain sodium carbonate or bicarbonate. In the use of these waters for boilers, their evaporation in the production of steam causes concentration of the impurities, and hence a gradually increasing sulfate and chloride content, and in the case of those containing sodium carbonate or bicarbonate, of carbonate and hydroxide content as well, the latter being due to the decomposition of sodium carbonate into caustic soda when in solution at boiler-water temperatures. In a water containing calcium and sulfate, the concentration of the latter will not become great as evaporation proceeds, because the solubility of calcium sulfate is readily exceeded, and it deposits as adherent scale on the heating surfaces, thus removing the sulfate.

In the treatment of waters to prevent formation of adherent scale, the chemicals used are, in general, lime and soda ash, soda ash alone, sodium chloride through the medium of the zeolites, or artificial products having their properties, or at high pressures, the phosphate radical either as phosphoric acid or one of its sodium salts. Whether the treatment is accomplished on the feed water and external to the boiler, or directly on the water in the boiler, the result is much the same as regards the amount of soluble solids dissolved in the boiler water. The removal of the scale forming constituents from the water leaves therein soluble salts, such as sodium sulfate, chloride, carbonate, hydroxide, which increase in concentration as evaporation proceeds, and exercise their influence in retarding the disruption of bubble-enveloping films in the steam drum. Whether the treatment is external or internal, suspended material of like type develops in the boiler water. As noted heretofore, the character of this material, and not its quantity, is of greatest significance in its effect on foaming.

From the standpoint of prevention of adherent scale, the concentrations of carbonate, phosphate and hydroxide which are essential in boiler waters have been summarized in my Patents Nos. 1,613,656 and

1,613,701 of January 11, 1927. Also there the relation of these concentrations to the sulfate concentration in the boiler water, and the operating pressure of the boiler have been described. And further therein, I have stipulated the concentrations of caustic alkali in the boiler water which are satisfactorily inhibitive to corrosive action on the surfaces of the boiler, and have designated means whereby the content of insoluble solids or suspended matter in the boiler water may be reduced as desired.

Inasmuch as the conditions for the prevention of adherent-scale growth and corrosion and the accumulation of suspended insoluble solids for high concentrations of soluble solids in the boiler water can be readily and economically controlled, the function of the boiler blow-down becomes that of so limiting the concentrations in the boiler water of sodium sulfate, sodium chloride, saponified material, etc., that the coalescence and disruption of the steam-enveloping liquid films throughout the boiler water and the steam-water interface shall occur with a rapidity compatible with the delivery of steam of suitable quality through the steam outlet.

In some plants, the use of evaporated make-up water limits the soluble and insoluble impurities in the boiler water mainly to those derived from condenser leakage, and in these plants, the amount of boiler blowdown requisite for satisfactory operation is very small. In many plants, however, such evaporation is not economical, and a large make-up of natural or treated water must be used. If the natural water contains a relatively small amount of impurities, the blowdown may be only nominal; but if it contains a large amount of impurities, the blowdown may be excessive for the boiler to deliver a good quality of steam.

However, I have found that certain conditions may be maintained in the boiler water and at the steam-water interface of the steam drum, which will negate the retarding effect of increasing concentrations of soluble and insoluble impurities in the boiler water on the coalescence and disruption of the liquid films enveloping the bubbles of steam, and thus effect their rapid coalescence and disruption.

I have found that when the hydrogen ion concentration of a boiler water is somewhat greater than that of pure water, so that, when cooled to room temperature its pH value is 4 or less, it may contain relatively large quantities of the impurities characteristically present in boiler waters, and yet show no signs of foaming. But such a condition cannot be maintained in a boiler water without damage to the boiler, inasmuch as at this concentration of hydrogen ion, the boiler metal corrodes rapidly. In fact, from the standpoint of corrosion, a slightly alkaline

boiler water is better than a purely neutral water. Thus an alkalinity of approximately 50 parts per million of hydroxide (OH) or more, the amount depending mainly upon the concentration of sulfates and chlorides in the boiler water, is satisfactory.

Under these concentrations of alkalinity, slow coalescence of the bubble-enclosing liquid films readily occurs in boiler waters, causing foaming. Experiments made by the boiling of water in open beakers or flasks will not show this effect readily, due to the presence of air at the steam-water interface. The conditions in a boiler are different from those of the open beaker or flask, in that substantially pure air-free steam is in contact with the surface of the water. Apparently the presence of a gas in the steam above the water tends to cause disruption of the bubble-enclosing liquid films, a condition which is not normally encountered in steam boilers.

In tests made on boiler waters synthesized from distilled water and pure chemicals, and on samples of boiler water obtained from boilers operating under diverse conditions, I have found that we may divide these waters into three classes according to the means which must be used to induce ready coalescence of disruption of the bubble-enclosing liquid films, as follows:

Class A consists of those boiler waters which contain calcium, barium or strontium salts, but only limited quantities of saponified material. The minimum quantity of the metal radicals noted which must be present in solution is represented by the concentration of calcium present in a water fully treated by soda ash as defined in my Patent No. 1,613,701, or its chemically equivalent amount of barium or strontium. The alkalinity of the water should be not less than 25 to 50 p. p. m. of hydroxide. This class therefore includes all boiler waters derived from waters which contain sodium carbonate or bicarbonate in their natural state, or treated by a zeolite or which are treated externally or internally by a hydroxide or carbonate as by lime, caustic soda, soda ash, barium hydroxide, barium carbonate or a combination thereof, unless they are seriously contaminated by saponified material.

In a boiler water of this character, the maintenance therein of a limited concentration of certain types of substances hereafter specified, or of the products derived therefrom by their chemical reactions with the hot boiler water, results in ready coalescence or disruption of the bubble-enclosing liquid films, even though the sulfate, chloride, hydroxide or carbonate, etc., concentration may reach relatively high values. Thus, the amount of blowdown necessary when satisfactory operation requires the maintenance of 2000 p. p. m. only of sulfates or chlorides in the boiler water may be reduced to that

necessary for the maintenance of 10,000 or 20,000 p. p. m. or more of sulfates or chlorides.

One type of substance which effects this result satisfactorily is tartaric acid (a dihydroxydicarboxylic acid) or the metallic salts or acid salts thereof. Another type of substance is citric acid (a hydroxytricarboxylic acid), and the metallic salts or acid salts thereof. The effectiveness is not as great as that of the preceding type of substance. A third type of substance is a trihydric phenol as pyrogallol; gallic acid, which on heating yields pyrogallol; and the tannins or tannic acids, which when boiled with dilute acids, as sulfuric or hydrochloric, yield gallic acid, and which are regarded as probably having the constitution of a pentadigalloylglucose. The tannins are widely distributed in the vegetable kingdom, and vary to some extent in their properties, but have the common property of yielding gallic acid when treated as stated. The metallic or acid salts of gallic or tannic acids are likewise effective. This third type of substance is the most effective of all.

The term "a tannin" is intended to include the various substances having the properties of tannin and to include gallic acid, pyrogallol and similar substances.

All of these substances have the anti-foaming effect of the tannins. They are, so far as my present investigations have shown, organic bodies of the general type above set forth, and in general, appear to be the hydroxy acids of the aliphatic series and the di- or tri-hydroxy acids of the aromatic series. These have an anti-foaming effect in connection with the hydroxyl radical and alkaline earth metal radicals, such as calcium. Apparently, the antifoaming effect of these substances is dependent upon the presence either naturally or by additions in the water, of an alkaline earth metal, such as calcium, barium or strontium, together with hydroxyl. Tests have indicated that the presence of all three of these substances namely, one of the antifoaming organic substances above mentioned, an alkaline earth metal and hydroxyl, are desirable, if not requisite for the prevention of foaming.

It is infeasible to control by tests on the boiler water the concentrations of these various organic anti-foaming substances in the boiler water which should be maintained for optimum results, inasmuch as analyses therefor are difficult, and also, at the temperature of the boiler water, decomposition may be occurring. A practical method for maintaining the effective concentrations in the boiler water is to dissolve the material in the feed water to a concentration which is fixed by the concentration to be carried in the boiler water, and the amount of blowdown of the boiler. The concentration of the tartaric,

gallic or tannic radical to be carried in the boiler water may vary from a minimum of approximately 25 parts per million to a maximum of about 100 parts per million, calculated on the basis of the substance as introduced depending upon the per cent of rating at which the boiler is operated, and the concentration of dissolved and suspended materials in the boiler water. Thus, if a concentration of 80 parts per million in the boiler water is advisable, and the boiler blowdown is 5% of the entering feed water, then the concentration of the tartaric, gallic or tannic radical in the entering feed water must be 4 parts per million; but if the blowdown is only 1%, then the concentration must be 0.8 parts per million. The amount of blowdown is readily obtained from a comparison of the chloride or sulfate concentrations of the boiler and feed water respectively, if not known by direct measurement.

The effectiveness of these organic anti-foaming substances in the presence of the concentrations of calcium, barium or strontium and hydroxyl, above noted is satisfactory. Also, the effectiveness of these substances does not diminish rapidly so that their introduction into the boiler water may be controlled as noted above. The control of the hydroxyl and alkaline earth metal concentration is effected as described in my application Serial No. 718,322.

The requisite concentration of these materials in the boiler water for satisfactory results may be readily judged by observations made on the temperature of the steam leaving the superheater or on the water in the gauge glass of the boiler. Thus if the temperature of the superheated steam is subject to sudden drops, or the water level is fluctuating violently, boiling conditions are unsatisfactory, and a higher concentration of the treating substances should be maintained. Or, if the amount of discharge from steam traps connected with steam purifiers attached to the steam outlet of the steam drum is excessive, the concentration of the treating substances should be increased within the limits heretofore defined.

If the addition of the treating substances within these limits does not produce satisfactory boiling conditions, then the boiler must either be blown down, as the allowable limit of saponifiable material has been overstepped in the boiler water, and no excess of treating substance can be effective; or a gas may be introduced in conjunction with these treating substances, as hereinafter described under Class C waters.

Class B consists of those boiler waters which contain less calcium, barium or strontium than that indicated as a minimum for the Class A waters, and which contain only limited quantities of saponified material. The waters of Class B, therefore, comprise

those in which the calcium content is very low as may be the case when the feed water is distilled water, and the only contamination of the boiler water arises from condenser leakage, or wet steam from the evaporator; or as occurs when the final conditioning of the boiler water is accomplished by the use of phosphate radical as described in my Patent No. 1,613,656.

Under these conditions, the types of substances designated for the Class A waters are very little, if at all, effective. On the other hand, the types of substances designated hereinafter as effective in negating retardation of coalescence or disruption of the liquid bubble-enclosing films for Class B waters, are likewise effective on Class A waters.

The fundamental substances which appear to be most effective on waters of Class B, are alcohols, particularly the monohydric alcohols. Their solubility in the boiler water must be slight. As they are all substances which volatilize in the steam, they should either be supplied continuously in small amount to insure their presence in the boiler water, or should have a relatively low vapor tension at the temperature of the boiler water. Some of the alcohols among others which have these characteristics are cetyl, ceryl, and myricyl alcohol; and the sterol alcohols, as cholesterol and phytosterol, which are all monohydric alcohols. These substances are not readily synthesized in the laboratory, nor do they occur in pure form in nature. Some of the more common materials from which they may be obtained by chemical treatment are as follows:

Myricyl alcohol from beeswax (various varieties contain different percentages of this alcohol) and carnauba wax.

Ceryl alcohol from Chinese insect wax, carnauba wax and wool fat.

Cetyl alcohol from spermaceti, which also contains other effective alcohols as dodecyl, tetradecyl and octadecyl.

Monohydric alcohols, as dodecyl, found in relative large percentage in sperm oil and arctic sperm oil.

Cholesterol, found widely distributed in the animal kingdom, in small percentage; in higher percentage in gallstones, wool fat (wool wax or lanolin), and the shark oils; and in small percentage in butter fat, egg oil, cod liver oil, and others.

The vegetable sterols, as the isomeric phytosterols, widely distributed in the vegetable kingdom, and found in small amounts in various oils derived therefrom, as cottonseed oil, corn oil, wheat oil, olive oil, and many others; also as a glucoside in olive bark and in nutmeg, taraxacum root and bryony root, and many others.

The alcohol, which is the desirable and effective component in these various natural substances, may occur uncombined, to some

extent, as myricyl alcohol in carnauba wax, but in general is found as the ester of an organic acid. Thus the cetyl alcohol exists in spermaceti as the ester of palmitic acid; myricyl alcohol in beeswax as the ester of palmitic acid; and ceryl alcohol in Chinese insect wax as the ester of cerotic acid.

If the natural substance, as beeswax, spermaceti, lanolin, or carnauba wax, is introduced into a slightly alkaline boiler water which is free from saponified material or contaminated therewith to a very limited extent, it is effective in speeding up the coalescence or disruption of the liquid films, because, as the alkalinity of the boiler water breaks up the esters into a salt of the acid and the uncombined alcohol, the latter is free to exercise its effect on the films. The salts of many of the acids, however, as stearic, palmitic, oleic, etc., are effective in stabilizing the films; and as the alcohol volatilizes with the steam while the sodium palmitate or other organic salt remains in the boiler water the final condition is worse than the initial. Finally, then, unless the blowdown is appropriate to avoid the condition, the accumulation of the salt derived by saponification of the ester becomes sufficient to nullify completely the effectiveness of the alcohol. Also, the hydrocarbons contained to some extent by most of the natural substances, and the saponification of the glycerides of the fatty acids therein seem to hasten the stabilization of the films.

Thus the regular use of the natural substances herein described may be made effective by their introduction into the boiler water continuously in small amount, in conjunction with an amount of blowdown sufficient to prevent too great accumulation of saponified material or hydrocarbons derived from the substance. Under these conditions, the use of carnauba wax is preferable to the use of beeswax, lanolin, and shark oil, because the saponified material collects less rapidly in the boiler water. The use of carnauba wax is preferable to the use of spermaceti and sperm oil for a like reason, and further because the alcohol of the former is less readily volatile in the steam than those from the latter two.

I prefer, however, to saponify the natural substance, and to extract therefrom the alcohol or alcohols, and thus introduce them into the boiler water in a condition of commercial purity, thereby avoiding the accumulation of saponified material.

The choice of alcohol to use is based on the operating pressure. Thus, the sterol alcohols are least volatile in the steam, and hence of greatest value at high operating pressures. At lower pressures, ceryl, cetyl, or myricyl alcohols may be entirely satisfactory, or even the more readily volatile alcohols from the sperm oils.

The amount of alcohol which much be con-

tinuously introduced into the boiler water depends upon the operating pressure of the boiler, the volatility in the steam of the alcohol used, the per cent of rating at which the boiler is operated, the concentration and type of dissolved inorganic salts and suspended matter in the boiler water, and the contamination thereof with saponified material. The amount required may be conveniently controlled by the smoothness of boiling as indicated by any sudden drops in the temperature of the superheated steam or fluctuations in the level of water in the gauge glass of the boiler, or by the amount of discharge from steam traps connected with steam purifiers attached to the steam outlet of the steam drum.

In the presence of saponified material, the substances specified under the Class B waters may be used in conjunction with the introduction of a gas, as hereinafter specified under Class C waters.

Class C consists of boiler waters which may conform to the conditions specified in either Class A or Class B as regards their concentration of calcium, strontium, or barium, but in which the concentration of saponified material is great enough to render unavailing without aid the effectiveness of the substances specified in the two preceding classes.

Under these conditions, I have found that the continuous introduction into the boiler water of a small amount of gas, as air, nitrogen, stack gas either without purification or purified of its sulfur dioxide and carbon dioxide, or natural gas, is very effective in decreasing the stability of the liquid films and hence hastening their coalescence or disruption. Especially is this true if the gas is introduced in the form of fine streams well distributed over and slightly below the steam-water interface.

The nature of the gas used is immaterial, so long as it does not remain in solution in the boiler water.

The effect of the gas is apparently to cause a greater partial pressure on one side of the liquid films of the bubbles than on the other side, and consequently, to tend to cause disruption or instability of the film. If there be only pure steam on both sides of the film, the equilibrium pressure and temperature on the two sides is the same, but if there be a greater partial pressure of the gas on one side of the film, there will be a greater total pressure on that side of the film, which will tend to make it unstable.

The quantity of gas used must be based upon the per cent of rating at which the boiler is operated, the amount of saponified material in the boiler water, the concentration and type of soluble salts and suspended matter therein, and whether it is used in conjunction with the materials specified as efficacious for Class A and Class B waters, or

without their aid. The maintenance of a sufficient supply of the gas is readily recognized by observations of the temperature of the superheated steam, by sudden fluctuations in the level of water in the gauge glass of the boiler, or by the amount of discharge from steam traps connected with steam purifiers attached to the steam outlet of the steam drum.

- 10 This use of a gas to produce instability of the liquid films, and hence a more rapid coalescence and disruption of the films, is not limited in its application to boiler waters, but may be made use of in all processes of
15 evaporation in which a slight difference in the partial pressure of the components on the two sides of the liquid film renders that film unstable. The control by its use of the purity of condensate in an evaporation of waste liquids may be cited as an example.

20 In these specifications the terms boiler and boiler water are not limited in their significance to the generation of steam at a pressure sufficient for power purposes, but have rather
25 the broader meaning of the boiling of a liquid in any closed vessel, as an evaporator.

In the practice of the invention, the use of the materials specified under Class A in conjunction with those specified under Class
30 B and/or Class C for waters of Class A may be found advisable at times. Likewise the use of gas in conjunction with the materials specified under Class B may be advisable also for Class B waters.

35 Claims directed particularly to the use of an alcohol or wax are presented in my application, Serial No. 283,456, filed June 6, 1928 as a division of this case.

While I have specifically described the preferred embodiment of my invention, it is to be understood that the invention is not so limited, but may be otherwise embodied within the scope of the following claims.

I claim:

45 1. The process of inhibiting foaming in steam boilers, comprising bubbling a small amount of insoluble gas through the steam-water interface.

50 2. The process of inhibiting foaming in steam boilers, comprising maintaining in the water a substance which accelerates the coalescence and disruption of the liquid bubble-films and introducing a small amount of insoluble gas into the water.

55 In testimony whereof I have hereunto set my hand.

RALPH E. HALL.

