

1

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**METHOD OF INHIBITING SLAG FORMATION IN BOILERS AND INHIBITOR MATERIALS FOR USE THEREIN**

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This invention relates generally to boiler slag inhibitors and a method of inhibiting slag formation in boilers. More particularly, the invention has special application to boiler slag inhibitors and a method of inhibiting slag formation in boilers fired with residual petroleum or other liquid hydrocarbon fuels, and to a method of introducing boiler slag inhibitors, either solely as a fuel additive, or in conjunction therewith to supplement the concentrations obtained as additives by physical injection of the inhibitors into the boiler flue gas streams.

The combustion of residual petroleum or other hydrocarbon fuels in boilers, both land based and marine, produces an ash which after fusion in the firing flames may remain sufficiently soft, plastic or molten to adhere to the steam generating surfaces and superheater tubes, or elsewhere on fireside surfaces, where a substantial amount of it may solidify in the form of a slag deposit. This deposit interferes with the transfer of heat and the flow of combustion gases, and thereby decreases the degree of steam superheat and generally reduces the efficiency of the other functions of the boiler.

As combustion continues, this adherent encrustation of slag builds up with the consequent deleterious effects of thermally insulating the tubes through which it is desired to conduct heat of combustion, and of tending to obstruct the passage of flue gases through the firesides of the boiler, so that at times the boiler may become practically inoperative after relatively short periods of operation.

The composition of this slag and consequently, its fusion characteristics and its tenacity will vary with the type and source of fuel as well as with the degree of contamination of the fuel, for example, by salt from sea water in the case of marine boilers.

In the case of boilers fired with residual petroleum fuels, and particularly in the case of marine boilers, this slag has generally been found to comprise primarily sulfates and vanadates of sodium, in their simple ortho as well as complex anionic forms, such as sodium sulfate, sodium acid sulfate, sodium pyrosulfate and sodium orthovanadate, sodium pyrovanadate, etc. Furthermore, these slags also may contain varying amounts of carbon and carbonaceous materials due to incomplete oxidation of the fuel.

It is a principal object of this invention to provide a method and means for chemical modification of the ash and other residual deposits of the combustion of fuels as described above to inhibit the formation of deleterious slag, and thus to improve the ultimate efficiency of such boilers by eliminating or retarding fouling of fireside heat transfer surfaces. It is also an object to provide means for introducing such inhibitors of slag formation into the fuel systems of boilers, and, specifically, into their flue gas systems to supplement or supplant slag inhibitors otherwise introduced. Additional objects and advantages of the invention will become apparent from the description that follows.

It has been found by test that the objects of this invention can be attained and that the ash and other

2

deposits resulting from the combustion of the usual fuels in steam generating boilers can be chemically modified to inhibit the formation of harmful slag deposits by the introduction with the fuel, or otherwise as will be later described, of combinations of chemical substances of specific characteristics as set forth below. Generally, the combinations of chemicals referred to include compounds of metals of two groups: First, metals whose oxides are refractory in nature and less basic than those of the alkali metals, and second, amphoteric metallic elements whose oxides in their higher states of valence are acid anhydrides less volatile than sulfur trioxide and which can displace sulfur trioxide from its alkali metal salts at elevated temperatures. For the purposes of this description, metals of the first group will be designated as M whose oxides have the general formula MO and this group specifically includes: magnesium, calcium, barium, strontium, nickel, cobalt and copper. Similarly, the amphoteric metallic elements of the second group will be herein designated as R and in combination with oxygen, these metals possess valences greater than 2, thus yielding oxides of the formula RO<sub>x</sub>, where x is greater than unity, for example, R<sub>2</sub>O<sub>3</sub>, RO<sub>2</sub>, R<sub>2</sub>O<sub>5</sub>, and the like. This second group of metals, designated R, specifically includes: aluminum, chromium, iron, manganese, molybdenum, titanium and zirconium.

Suitable combinations of the metals of groups M and R may be conveniently added to liquid hydrocarbon fuels in the form of oil-soluble organo-metallic complexes of various types, for example, as chelates of polyfunctional ketones, such as 2,4 pentanedione, or as related types of compounds formed by interaction with hydroxy or keto carboxylic acids, or as naphthenates or as salts or soaps of substituted or unsubstituted fatty acids of various types, or as mixtures of these. It is not necessary that pure or specific organo-metallic compounds be employed since the prime requisite is provision of the proper quantity of the metals in the correct ratio and preferably in a suitably oil-soluble form. This fact, therefore, enables the invention to be practiced economically through the use of mixtures of oxygenated complexes, such as those formed by the partial oxidation of light petroleum fractions, which, on interaction with salts of the specified metals, form oil-soluble organo-metallic compounds that may range from simple salts of carboxylic acids to chelated complexes of polyfunctional hydroxy, keto and carboxy compounds whose exact structure has not and need not be determined.

It is also possible to employ the slag inhibitor metals of this invention by their addition to the fuel in solid powdered form, as their oxides or as salts which give rise to the oxides referred to on combustion of the fuel, and to suspend the powdered mixture of metal compounds in the fuel prior to its combustion. Also, to supplement or, in some cases to replace, the introduction of the inhibitor metal with the fuel, it may be desirable to apply the inhibitor metal combinations at a point in the boiler flue gas system where the inhibitor will be carried with the flue gases to those surfaces of the boiler firesides most susceptible to slag formation, usually the steam superheater tube surfaces. These alternative methods of application of the slag inhibitors of this invention will be hereinafter further described in detail.

Regardless of the mode of their introduction into the fuel combustion system of a boiler, the slag inhibitors of this invention serve to eliminate or to minimize the formation of adherent slag deposits on the fireside surfaces of steam generating boilers.

The precise manner in which the inhibitors of this invention act to perform their function cannot be stated with certainty, and it will be understood that the invention is not to be regarded as restricted in any manner to pos-

sible theoretical explanations advanced, but it is intended in scope to be commensurate with the results achieved in the practice of the invention. With this in mind, it may be postulated that the effective action of the inhibitors described is due to the formation of a refractory surface film of high fusion point on the droplets of molten ash that prevents the accumulation of adherent deposits on fireside surfaces of the boilers. For example, when appropriate combinations of metals selected from the previously identified groups M and R are subjected to the temperatures of fired combustion in a boiler they are converted to their respective oxides, MO and RO<sub>x</sub>. These oxides further interact to form complexes having high fusion points, high densities, and, when solid, a high degree of hardness. These complexes of refractory metal oxides with oxides of amphoteric metals can be generally classed as spinels, of which the characteristics of many are known. The dispersion of these complexes or spinels in the combustion or flue gas systems of a boiler is essentially molecular, and the complexes are adsorbed on the surface of the far larger quantities of molten ash resulting from combustion of the fuel. Because there are only minor forces of diffusion involved between the molten ash and the adsorbed spinel complexes, the latter tend to remain largely at the surface of the molten ash deposits, and thus interpose an interface or film of greatly higher fusion point between ash and the fireside surfaces within the boiler. As a result of the elevation of the fusion point of at least the surface of the particles of ash above the temperatures existing at the heat transfer surfaces of the firesides of the boiler, there is virtually no adhesion of the ash to such surfaces, and consequently no deleterious accumulation of slag deposits.

It is also noteworthy that the addition to the fuel of compounds of one or more of the metals from only one of the groups M and R is substantially ineffective to produce any appreciable effect on the accumulation slag. For example, if one or more of the compounds resulting on combustion in the refractory oxides of the metals involved, viz. having the general formula MO, is added to the fuel, only a negligible elevation of the fusion temperature of the molten ash droplet surfaces results with a virtually imperceptible effect in preventing adherence of the ash droplets to the boiler heat exchanging surfaces. Moreover, addition to the fuel of one or more of the compounds which result only in the formation of the amphoteric oxides of the formula RO<sub>x</sub> has no effect in raising the fusion temperature of the molten ash since these oxides themselves have low melting points. It is only in the interaction with one another of one or more of the oxides of each type, that high fusion point products are obtained with effective results in inhibiting adherence of the molten ash and consequent formation of slag.

As referred to above, it is necessary to maintain proper proportions of the metals of each of the two groups named; the ratio of the additives of each type must be controlled within fairly close limits. To produce on combustion and interreaction with each other a spinel complex of the desired high melting point, it is preferable to produce substantially numerically equal molecular quantities of each type of oxide. However, inhibitors of only slightly lower melting points may be more economically produced and with less rigid control than is required to maintain equal molecular quantities of each type of oxide by carrying out the combustion and interreaction of the oxides with a potential excess of the more refractory oxide. Under these conditions, equal molecular quantities of the oxides of each type tend preferentially to interreact to form first the highest melting-point spinel structure which is then somewhat reduced by the surrounding matrix of the potential excess of the more basic refractory oxide.

The concentration of the combined additives of each

type in solution in the fuel has been found to be effective in the elimination or suppression of slag when employed in the range of from 1 to 100 parts by weight of total additive metals (as the elements) per million parts of fuel.

Examples of the method of slag inhibition obtained by the interaction of metal oxide-amphoteric oxide compounds which may be synthesized by the oxidation of mixtures of additives of the two types dissolved in or mixed with the fuel and their subsequent interreaction follows:

## I

To one million parts of heavy, bunker C type oil fuel were added 2.55 parts of zirconium in the form of an oil-soluble organo-metallic compound, namely, the zirconium salt of alpha-hydroxy duodecenoic acid and 2.45 parts of strontium in the form of the strontium salt of the same acid. There was thus present a total of 5 parts by weight per million of the two metals. On combustion of the fuel the oxides of these elements in their higher states of valence are formed. These oxides react with each other to form a strontium zirconate having a fusion point in excess of 2700° C. (4900° F.), which is higher than the fusion point of either of the pure oxides alone.

The degree of dispersion of this compound on its formation in the flue gases appears to be essentially molecular or microcrystalline, and it is adsorbed on the surface of the molten ash formed on the combustion of the fuel, where it tends to remain. The fusion point of the surface film of the molten ash, rich in strontium zirconate, is thus elevated to a temperature higher than that existing at the metal heat transfer surfaces of the boiler and adhesion and agglomeration of the ash is thus inhibited or prevented.

## II

To one million parts of heavy, bunker C type oil fuel were added 5 to 9 parts by weight of magnesium in the form of the magnesium salt of alpha hydroxyduodecenoic acid and from 1 to 5 parts by weight of aluminum in the form of the salt of the same acid, the combined quantity magnesium and aluminum totalling 10 parts per million.

On combustion and interaction of the resulting metal oxides, there appeared to be formed a solution of magnesium aluminate spinel in magnesia, the fusion point of which is in the range of 2200° to 2700° C. Acting apparently in the manner previously described, this complex was effective essentially to eliminate the cohesion and adhesion of molten ash to fireside surfaces.

The ratios for the two types of metals set out in the examples are those preferred, but operable ratios have been found to exist between limits of 10% and 90% of either type of metal compound and which comprises proportions varying widely from the stoichiometric requirements in a spinel matrix corresponding to the general formula MO.RO<sub>x</sub>.

Additional examples illustrating the invention may be presented in tabular form as follows:

Table

| Refractory Oxide (MO) | Amphoteric Oxide (RO <sub>x</sub> ) | Parts/million By wt. in fuel | Melting Point, Spinel-Slag, ° F. |
|-----------------------|-------------------------------------|------------------------------|----------------------------------|
| BaO                   | Al <sub>2</sub> O <sub>3</sub>      | 5-20                         | 3,300                            |
| FeO                   | Al <sub>2</sub> O <sub>3</sub>      | 14-20                        | 2,900                            |
| FeO                   | CaO                                 | 10-22                        | 3,850                            |
| MgO                   | Al <sub>2</sub> O <sub>3</sub>      | 4-10                         | 3,775                            |
| MgO                   | Fe <sub>2</sub> O <sub>3</sub>      | 8-32                         | 3,200                            |

In this latter group of five examples, the cohesion and adhesion of the molten ash was found on combustion of the fuel to be largely eliminated, and the ash deposits were found to be flaky, easily removed and reduced in

quantity by comparison with those resulting from combustion of the same fuel without the additives described.

The slag inhibitors of this invention may be introduced into the boiler in almost any manner, but from a practical standpoint one of the methods described below is preferably employed.

As shown in the examples above, oil-soluble metallo-organic compounds of the metals may be formed, in which event it is only necessary to dissolve the specified amount of the material in the fuel prior to its combustion. However, if it is desired to provide the inhibitor in dry or powdered form for reasons of storage or the like, a small pre-mixing tank may be employed wherein the inhibitor compounds in powdered form can be agitated with a portion of the fuel or another suitable carrier to produce a suspension, which is then added in proper quantity to the fuel feed to the boiler.

In either case, the inhibitor is added directly to the fuel and in this manner, as the fuel is burned, the inhibitor oxides are carried with and deposited by the flue gases on the various fireside surfaces where slag formation and accumulation would otherwise occur. In most instances it will be found that this type of application will suffice. However, there may be instances where peculiarities of the boiler structure or its manner of operation make it necessary or desirable to supplement the amounts of inhibitor introduced as additives with the fuel. Since the superheater tubes are generally the point of greatest slag congestion due to their closely nested construction, it has been found that where supplementary application of slag inhibitor is indicated, it should preferably be introduced into the flue gas stream near the superheater nests. A convenient manner of application is afforded by means of auxiliary equipment known as "soot blowers" generally located in at least this general area of the flue gas stream in most boilers. In this instance, the inhibitor compounds of this invention, either in hydrocarbon or in aqueous solution, or in the form of finely divided solids, may be supplied periodically through the soot blowers by means of a timing cam set by suitable means to discharge inhibitor material into the flue gas stream for brief periods, for example, of from 30 to 60 seconds, at intervals adjustable between wide limits, or in response to manual operation of the soot blowers. In this manner supplementary amounts of slag inhibiting material can be made to exert their beneficial action by distribution through the boiler with the flue gas stream to those surfaces which require greatest protection.

It will be apparent to those skilled in this art that various modifications of the methods and compositions described are possible within the general limits of the invention set forth, and such modifications are intended to be included within the scope of this invention as defined by the appended claims.

I claim:

1. Method of inhibiting the formation of slag on the firesides of boilers, which comprises entraining in the boiler flue gas stream resulting from the combustion of fuel in the boiler at least one basic metallic oxide less basic than oxides of alkali metals in combination with at least one amphoteric metallic oxide that in its higher valence state forms an acidic anhydride capable of displacing sulfur trioxide from sodium sulfate at elevated temperatures, said oxides being present in said boiler flue gases in substantially equal molecular quantities, the total quantity of said oxides being from 1 to 100 parts per million parts of the fuel.

2. Method of inhibiting the formation of slag on the firesides of boilers, which comprises entraining in the boiler flue gas stream resulting from the combustion of fuel in the boiler at least one basic metallic oxide less basic than oxides of alkali metals in combination with at least one amphoteric metallic oxide that in its higher valence state forms an acidic anhydride capable of dis-

placing sulfur trioxide from sodium sulfate at elevated temperatures; the total quantity of said oxide being from 1 to 100 parts per million parts of the fuel, and the proportion of oxide of each type being from 10% to 90% of the total, the reaction of said oxides to form a spinel in association with molten ash resulting from combustion of the fuel being effective to elevate the fusion point of said molten ash sufficiently to inhibit substantially the agglomeration of said ash into slag.

3. Method of inhibiting the formation of slag in the firesides of boilers in which petroleum fuels are burned, which comprises entraining in the boiler flue gas stream resulting from the combustion of said fuels at least one basic metallic oxide less basic than oxides of alkali metals and having the general formula  $MO$  where  $M$  represents the metal in combination with at least one amphoteric metallic oxide that in its higher valence state forms an acidic anhydride capable of displacing sulfur trioxide from sodium sulfate at elevated temperatures and having the general formula  $RO_x$  where  $R$  represents the metal and  $x$  is greater than unity, and reacting said oxides upon molten ash deposits on the boiler firesides resulting from combustion of said fuel to form relatively high melting point spinels of the general formula  $MO.RO_x$  whereby agglomeration of said molten ash into slag is effectively inhibited, the total quantity of said oxides being from 1 to 100 parts per million parts of said fuel.

4. Method of inhibiting the formation of slag on the firesides of boilers in which hydrocarbon fuels are burned, which comprises the steps of adding to said fuel a compound of at least one metal whose oxide is basic and refractory selected from the group consisting of magnesium, ferrous iron and strontium, and a compound of at least one amphoteric metal whose oxide in its higher valence state is an acidic anhydride selected from the group consisting of aluminum, ferric iron, cerium and zirconium, each of said metal compounds being present in amount equal to from 1 to 100 parts of the metal per million parts of said fuel, and burning said fuel containing said metal compounds to entrain the oxides of said metals in the resulting boiler flue gas stream and to react said metal oxides on molten ash deposits in the boiler to raise the fusion points of said ash sufficiently to inhibit agglomeration of said ash into adherent slag deposits on the firesides of the boiler.

5. Method according to claim 4, including the step of supplementing the quantities of said oxides entrained in said boiler flue gas stream on combustion of said fuel by periodically introducing additional amounts of said metal compounds directly into said boiler flue gas stream during its passage through the firesides of said boiler.

6. Boiler fuel slag inhibitor composition comprising from about 10% to 90% of a compound of at least one metal of the group consisting of magnesium, ferrous iron and strontium, in combination with from about 90% to 10% of a compound of at least one metal of the group consisting of aluminum, ferric iron, cerium and zirconium, said compounds comprising oxides of said metals and capable of forming reaction products at boiler flue gas temperatures which are spinels of high fusion points.

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