United States Patent Office 3,514,273 Patented May 26, 1970

3,514,273

FUEL OIL ADDITIVE

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No Drawing. Continuation-in-part of application Ser. No. 648,241, June 23, 1967. This application Nov. 25, 1968, Ser. No. 778,799

Int. Cl. C10l 1/32

U.S. Cl. 44—51 13 Claims

ABSTRACT OF THE DISCLOSURE

A fuel oil additive, which is designed to reduce slagging, to facilitate removal of slag and like deposits from the fireside of boiler tubes, to reduce acid smut pollution, to eliminate low temperature corrosion and to improve the electrical resistivity of particulate emission from a fuel oil flame, comprising a dispersion of finely divided particles or partially dehydrated hydroxides of magnesium and aluminum in a hydrocarbon oil.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of Ser. No. 648,241, filed June 23, 1967, and now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

The invention is in the field of slag, acid smut pollution and low temperature corrosion inhibiting additives for fuel oil (acid smut is defined as carbon soot that has adsorbed SO_3 and becomes corrosive when cooled below acid dew-point temperature that may range from 350° F. to 140° F.).

Description of the prior art

The use of fuel additives to prevent fouling and corrosion of gas turbine blades, and slag build-up, corrosion of both high- and low-temperature heat transfer surfaces and the like in coal and oil fired boilers have been the subject of research.

Proposals have been made for solution of gas turbine problems wherein conditions differ from those existing in coal and oil fired boilers. For instance, U. S. Pat. 3,002,826 proposes use of an additive in the form of an emulsion, the water phase of which is an aqueous solution of a salt of Al, B, Cu, Si or Zn, and the oil phase of which is a mineral oil. U.S. Pat. 3,067,018 relates to use of a specially formed emulsion of an oxide, hydroxide or carbonate of the metals of group II of the periodic system.

A proposal for solution of slag build-up in coal-fired boilers is the subject of U.S. Pat. 3,004,836 which relates to the use of a ground magnesia-phosphate mixture.

U.S. Pat. 3,036,901 proposes the use of a finely divided, oil-insoluble metallic additive which is initially suspended in a hydrated calcium acetate gel before being blended with a residual fuel oil carrier.

U.S. Pat. 2,845,338 proposes use of an additive comprising a mixture of a magnesium compound and a compound of Cu, Co, Mn, Fe or Ca.

SUMMARY OF THE INVENTION

The invention broadly resides in a fuel oil additive which comprises a dispersion in a hydrocarbon oil of finely divided particles of partially dehydrated hydroxides of magnesium and aluminum in a petroleum oil containing an anionic or non-ionic surfactant, the weight ratio of magnesium:aluminum being at least 1:1, said hydroxides having a minimum bound water content of about 0.5% by weight and a maximum bound water content of about 15% by weight.

The additive of the invention may be applied to package or field-erected commercial, industrial, power utility and heat recovery boilers, as well as to many fuel oil fired processes. The additive, when applied to a fuel oil in a suitable amount, has been found to (a) alleviate high temperature slagging and corrosion, (b) neutralize and dry up gummy, corrosive deposits at the cold end of a boiler or the like, (c) reduce the level of SO_3 and nitrogen oxides in the flue gases, (d) prevent the formation of acid smut, and (e) make it possible to control the emission of soot to the atmosphere.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the invention, finely divided particles of partially dehydrated hydroxides of magnesium and aluminum are suspended or dispersed in a petroleum or hydrocarbon liquid carrier with an anionic or non-ionic surfactant.

The partially dehydrated hydroxides may be described as a compound mixture of oxides and hydroxides having the general formulae $Mg_{II}O.OH$ and $Al_{III}O.OH$. The elemental magnesium present in the final mixture is not less than equal to the amounts of elemental aluminum in the mixture. A satisfactory weight ratio of Mg:Al for most industrial applications is from 1:1 to about 10:1. The additive active ingredients should contain about 0.5 to about 15% by weight of bound water. A restricted range of 0.5 to 5% by weight of bound water has been found to be quite satisfactory.

The partially dehydrated hydroxide particles, which range from 1 to 7 microns in size, are predominantly granular in shape to prevent erosion and plugging of fuel oil handling and atomizing equipment. The partially dehydrated hydroxide of magnesium is preferably obtained from sea or salt water because of its low abrasiveness and high chemical reactivity. Moreover, the mentioned particle size acts to control the physical structure as well as the quantity of material that deposits in both hot and cold regions of the boiler. Structurally, these particles are characterized by high specific surface areas varying from 400 to 1400 square meters per gram to maximize chemical reaction with combustion residues in gas, vapor and liquid state. The diameter of the pores permeating each particle should be at least 17 Angstroms and preferably range from 17 to 20 Angstroms for optimum physical adsorption of gas-phase pollutants.

It is pointed out that the stated particle size, pore size, and surface area are achieved by partially dehydrating the hydroxides of Mg and Al under closely controlled time-temperature conditions to the specified bound water content. It will be appreciated that the partially dehydrated hydroxides of the present invention have a physical structure completely different from that of the corresponding oxides and fully hydrated hydroxides. Aluminum oxide, for instance, has a crystalline structure which is so abrasive as to render it quite unsuitable, from a practical point of view, as a fuel oil additive because of its destructive erosion effect on equipment such as pumps and the like. If the hydration is too great, stable suspensions of pumpable viscosities cannot be achieved with economical amounts of surfactant.

The magnesium active ingredient of the present invention, by virtue of its specific physical properties, readily reacts with and chemically neutralizes any condensed acid. On the other hand, the aluminum active ingredient increase the effectiveness of any unreacted magnesium active ingredient that deposits on boiler surfaces by ensuring a highly porous (extended) surface layer for acid reac-

tions. Therefore, the net effect of using both magnesium and aluminum forms in the additive results in benefits due to the superposition of both physical adsorption and chemical neutralization processes.

Although the present invention is based upon the particular development of an additive having specified characteristics, the general knowledge that the various oxides and hydroxides of Mg and Al vary greatly in physical structure and chemical reactivity have been well-recognized in the past.

For instance, a paper entitled "Lilco Trims Residual Oil Problems" (L. M. Exley, A. E. Tamburrino and A. J. Neal, Jr., Power Magazine, April 1966) reported that:

"These experiences with MgO are somewhat paradoxical: Three types of MgO additives gave poor results, while a fourth type produced good results. A probable explanation is that the fourth is smaller in particle size, thus offering a larger surface for reaction with oil ash sulfates of low-temperature boiling point. And, since it is injected with the fuel oil, there is assurance that the MgO is available in the flame envelope where oil ash is greatest in concentration and turbulence is present for thorough mixing. Finally, no water is admitted with the MgO, as was the case with the slurry."

Another paper entitled "Effect of Fuel Oil Additives on Oil-Ash Corrosion and Deposits" (R. C. Amero, A. G. Rocchini and C. E. Trautman, ASTM Technical Committee, E Symposium, Jan. 28, 1964, Atlantic City, N.J.) shows that different forms of Mg and Al additives tested under nearly identical conditions yield widely divergent results. The paper contains the following data,

Additive	Additive-vanadium, wt.-ratio	Corrosion, mg./sq. in.	Deposits, mg./sq. in.
MgO	Mg/V=3/1	8	125
MgO	Mg/V=3/1	31	70
Mg metal	Mg/V=2.8/1	3	64
$Mg(OH)_2$	Mg/V=2.8/1	125	46
Organic Mg	Mg/V=3.2/1	+9	84
$MgSO_4$	Mg/V=2.8/1	74	137
Al_2O_3	Al/V=1.6/1	131	275
Organic Al	Al/V=2.1/1	840	131

These papers show that both the mineral composition and physical structure of each magnesium additive strongly influence its ability to control deposits and corrosion due to residual oil ash, even though the various magnesium materials should, by elementary reasoning oxidizes in the flame and deposit as MgO. The tests given in the Amero et al. paper indicate corresponding results with two Al compounds.

The specified partially dehydrated hydroxides of the present invention are, as previously indicated, suspended or dispersed in a carrier liquid which is preferably a light hydrocarbon oil having a maximum viscosity of 35 SSU at 100° F.

The surfactant, which is anionic or non-ionic and compatible with both of the active ingredients and the hydrocarbon carrier, transforms the highly viscous, two-phase mixture into a free-flowing easily-pumpable suspension that blends readily with fuel oil. Suitable surfactants are readily available. For example, the glycerol stearates and laurates and the heavy metal soaps of stearic, naphthenic and rosin acid, are particularly suitable. Examples of specific surfactants are glycerol monostearate (as sold under the trade name "Aldo 33" by Glycol Products Company); lecithin (as sold under the trade name "Clearate" by W. A. Cleary Corporation); sorbitan monolaurate, sorbitan tristearate, and glycerol sorbitan laurate (as sold under the trade names "Span 20," "Span 65" and "G–672," respectively, by Atlas Powder Company); fatty acid type such as that sold under the trade name "TDO" by Armour & Company; and heavy metal soaps, such as aluminum stearate, produced by reaction of a water soluble soap with a heavy metal salt of aluminum, magnesium, cobalt, zinc, manganese, or calcium. These surfactants also disperse and stabilize the solids in suspension by eliminating attractive forces on the particle surfaces. The surfactant is employed in concentrations ranging from 0.7% to 3.5% by weight.

The specified bound water content range is quite significant. As this content approaches zero the viscosity decreases but below about 0.5% the water is difficult to remove and the material becomes too expensive. Moreover, below about 0.5% desired physical characteristics are almost impossible to achieve. The product becomes difficult to disperse, it may become erosive, and higher drying temperatures are needed.

Above about 15% bound water content the viscosity is too great (approaching paste consistency), more surfactant is needed with consequent lack of economy, and it is difficult to achieve economical loading of the additive.

The final oil-base additive composition is a stable suspension having about 40–60% by weight of the active additive ingredients and a viscosity of less than 115 SSU at 80° F. Other physical characteristics may be listed as:

Specific gravity at 70° F.—1.35
Flash point (PM), ° F.—150 minimum
Pour point, ° F.— —10 maximum

Alleviation of high temperature deposits and corrosion

Laboratory experiments, using a combustion rig closely simulating field conditions, have shown that the additive described is particularly effective in changing the normally rock-like fuel ash slag into a porous, friable, powdery deposit that is easily removed by routine soot-blowing procedures. The deposit build-up with the use of the additive is loosely bonded to boiler tube surfaces and weakly agglomerated.

The deposits produced when using the additive were subjected to an intensive thin section investigation to clarify the role of additive properties, such as mineral composition and physical state, in preventing slag formation. Microscopic examinations of deposit thin sections showed a thin, dense unsintered layer of sub-micron particles next to the tube surfaces. Subsequent deposits formed an intermediate upstream layer of friable, moderately porous material, an outer upstream layer having a thick, porous, wedge-shaped structure and an outer downstream layer of powdery, moderately porous, lightly sintered crystals.

By optical and X-ray diffraction methods, it was determined that a magnesia-alumina reaction product, known as spinel, was uniformly distributed throughout all four layers and that the proportion of magnesium sulphate to magnesium oxide increased progressively toward the tube surface. The work also revealed that most of the vanadium was concentrated in the intermediate upstream and the outer downstream layers as bands of sodium vanadyl vanadate and magnesium orthovanadate. The partially dehydrated magnesium hydroxide component, therefore, prevents slagging of low-melting sodium and vanadium compounds by both mechanical dilution and chemical reaction.

The partially dehydrated aluminum hydroxide component also plays two important roles in modifying the slag structure. First, alumina, by reacting selectively with magnesia in the flame to form spinel, reduces the magnesia available for later reaction with sulphur oxides on the tube surface; this dictates the elemental magnesium to aluminum ratio for particular combustion conditions. The formation of magnesium sulphate, which is molten and sticky at 2050° F. should be minimized, particularly when gas tempertaures at the furnace exit are above 2100° F.; this is accomplished by increasing the aluminum active ingredient in the additive. Second, the magnesia-alumina reaction product reduces the tendency of unreacted but superfine magnesia particles to agglomerate. This control over agglomeration is probably due to the presence of uniformly distributed spinel particles that form cubic crystals of octahedral shape.

Porosity measurements on deposit samples also revealed that high porosity and large voids were specific to partially dehydrated hydroxides of magnesium and aluminum having particle sizes ranging from 1 to 7 microns. Control of particle size is important because theoretical studies showed that particles larger than 10 microns tend to form undesirably, densely impacted deposits. On the other hand, particles less than 0.5 micron tend to form undesirable cohesive deposits having small voids.

The additive of the present invention is thus suitable for controlling slag deposits on boiler surfaces over a wide range of gas temperatures. Furthermore, by preventing slag formation on tube surfaces, high temperature oil ash corrosion becomes impossible so that tube temperatures may be safely maintained at 1100° F.

To supplement the laboratory research, two power utility companies conducted field trials with additive formulations developed in accordance with the invention. In both cases, the boilers involved were rated at 360,000 lb./hr. of steam at 900 p.s.i.g. and 900° F.

Previously, these boilers were plagued with expensive maintenance and repair costs due to slagging and blocking of superheater elements every 4 to 6 weeks. Several proprietary anti-slagging additives had been tried during a four-year period but all were expensive and ineffective.

The additive employed in the trials as described in this application was used at a dosage rate of 1 gallon of additive per 1500 gallons of fuel oil, and had the following specific formula and characteristic,

Magnesium:aluminum—element wt. ratio	10:1
Particle size range, μ	1–7
Specific gravity at 70° F.	1.35
Flash point, (PM), ° F.	150
Pour point, ° F.	−10
Solids content, percent by weight	48

After four weeks of operation with this additive formulation (a) the hard, bonded slag build-up was replaced with a soft, friable powder that was easily removed by soot blowing, (b) bridging in the convection pass of the generating bank was eliminated, and (c) a light coating of additive oxides on the furnace walls was credited with raising superheat temperatures to design conditions for the first time.

A shipboard trial has also been made with an additive as described above but with a magnesium:aluminum ratio of about 1:1.

The ship's boilers being used for this trial suffered from severe superheated slagging because of their stringent design conditions. Typical boiler operating data are:

(a) 2500° F. gas temperature at the superheater,
(b) 975° F. superheater tube temperature, and
(c) 500 p.s.i.g. steam pressure from 5% to 125% of rated steam flow.

This trial is being conducted with an additive dosage rate of 1 gallon per 1000 gallons of fuel oil and information, supported with photographs, received from the ship indicates that superheater slagging has been successfully suppressed.

From results of the aformentioned laboratory experiments and field trials, it is concluded that the following additive formulaions and dosage rates are effective in preventing deposition and corrosion due to molten oil-ash constituents:

Furnace Exit temp., ° F.	Additive formulation, mg./Al ratio	Additive dosage rate gal./gal.
1,850 or less	10:1	1:1800
1,850–2,150	5:1	1:1500
2,150–2,450	3:1	1:1200
2,450 or over	1:1	1:1000

Control of low temperature deposits and corrosion

Laboratory combustion rig experiments have been conducted with the following formulation:

Magnesium:aluminum—element wt. ratio	2:1
Particle size range, μ	1–7
Specific gravity at 70° F.	1.35
Flash point (PM), ° F.	150
Pour point, ° F.	−10
Solids content, percent by wt.	48

These experiments have demonstrated that the fuel-oil additive invention reduced sulphuric acid corrosion on low-temperature boiler surfaces by 35% to 66% depending on the additive dosage rate. Laboratory studies have also indicated that a thin, uniform layer of active ingredients deposits on cold end surfaces by a process of agglomeration where they soak up and react with any condensed acid. The residue, after reaction with acid, consists mostly of water-soluble, non-toxic hydrated magnesium and aluminum sulphates that are easily removed by brushing or water-washing.

In related laboratory research experiments, it has been established that time-temperature conditions in industrial flames are not severe enough to dehydrate the active ingredients completely. Furthermore, partial rehydration between the active ingredients and water vapour in the flue gases occurs in the low-temperature region of the boiler. This rehydration phenomenon, by replacing evaporated hydroxyl groups, enhances the chemically basic properties of the magnesium active ingredient and ensures that the aluminum active ingredient will react with acid. The use of completely dehydrated aluminum oxide either amorphous or crystalline is avoided because chemical rehydration and acid neutralization reactions do not occur.

Field trails have also been conducted, using the following formulation:

Magnesium:aluminum—element wt. ratio	10:1
Particle size range, μ	1–7
Specific gravity at 70° F.	1.35
Flash point (PM), ° F.	150
Pour point, ° F.	−10
Solids content, percent by wt.	60

These trials were conducted in a number of power utility boilers that expeirenced serious cold end fouling and corrosion problems. In all trials the additive was initially applied to the rate of 1 gallon per 1500 gallons of fuel oil, after which the dosage rate was gradually reduced to 1 in 1800.

At the end of 8 weeks operation with additive-treated oil, the draft loss across the airheater of each boiled was unchanged; this indicated that frequent and periodic plugging of the tubular airheaters was no longer a problem. Inspection of the airheaters revealed that the active additive ingredients had completely dried up the original gummy, corrosive cold end deposits and that the thin coating of additive material on the tube surface was loose and powdery.

The boilers, which are now operating regularly on additive treated fuel oil, no longer require soot-blowing in the airheater zone and regular bi-monthly boiler outages for cleaning and replacement of airheater elements have been eliminated. The extremely low rate of increase in draft loss across the airheaters of these boilers indicates that cleaning of fireside surfaces can be programmed to coincide with annual boiler maintenance.

In one field trial an additive formulation containing a magnesium to aluminum ratio of 10 to 1 resulted in a 90% reduction of SO_3 in the stack gases when applied at the rate of 1 gallon per 1800 gallons of fuel oil. During this trial, SO_3 levels were reduced from 30 p.p.m. to 3 p.p.m. and the white acid plume from the stack was eliminated.

Abatement of acid smut emission

Another benefit from using the fuel-oil additive invention has been the abatement of acid smut emission. Without using the additive, acid smut, or soot soaked with sulphuric acid normally builds up in the cold end of a boiler or process and on the stack lining to some equilibrium thickness, after which it suddenly breaks free. Following emission to atmosphere these corrosive, sticky flakes of acid smut fall on people and property creating a serious nuisance problem and, in some cases, considerable damage to fabrics, crops and automobile finishes.

In large oil-fired boilers, exit gas temperatures often fall below the acid dewpoint. When this occurs and the additive is not used, electrostatic precipitators must be bypassed because of the potential fire hazard from the wet, combustible acid smut that is usually present. In such cases, smut emission is particularly bad, atmospheric pollution ordinances are frequently violated, and many complaints are commonplace.

This problem was eliminated entirely in one power utility boiler by applying the additive formulation containing an elemental magnesium to aluminum ratio of 10 to 1 at the rate of 1 gallon per 1500 gallons of fuel oil. Furthermore, the electrical resistivity of the solid residues leaving the boiler was improved to the extent that particulate matter can now be collected by the electrostatic precipitators. This solid residue, being dry and powdery, is also easily removed from boiler and dust collector hoppers.

In another power utility boiler the additive formulation containing an elemental magnesium to aluminum ratio of 10:1 was applied at the rate of 1 gallon per 1500 gallons of fuel oil for the purpose of controlling acid smut pollution low temperature corrosion. Reports on the results of this trial state: "The effect of the chemical's use are visible, both from a distance and at the station themselves. Most days the air above the stacks is free of what used to be the normal dark plume, and the area around the stations is practically free of fly ash fall-out . . . Even more important to the generating station operators, the soot and slag no longer clog up the huge airheaters connected to the furnaces. Normally, those units, which heat the air that's used in the boiler for combustion purposes, had to be washed out every six weeks . . ."

The fuel-oil additive described herein provides an economic means of controlling or eliminating boiler operational problems due to incombustible constituents in residual fuel oil. Economic benefits from using the additive include increased boiler availability and efficiency, reduced maintenance and fuel costs, and, in some cases, a financial credit on the sale of vanadium-rich ash collected in boiler and dust collector hoppers. Another major, but less tangible benefit, is the favourable public image created by minimizing the emission of noxious atmospheric pollutants.

The additive, which is normally metered continuously and automatically into the oil supply to each burner, can be formulated to the specific requirements of a particular boiler. Additive dosage rates will vary according to fuel analysis and combustion conditions, but usually 1 gallon per 1500 gallons of fuel oil is sufficient to control most problems at the cold end of a boiler or the like.

We claim:

1. A fuel oil additive which comprises a dispersion of finely divided particles of partially dehydrated hydroxides of magnesium and aluminum in a petroleum oil containing an anionic or non-ionic surfactant, the weight ratio of magnesium:aluminum being at least 1:1, said hydroxides having a minimum bound water content of about 0.5% by weight and a maximum bound water content of about 15% by weight.

2. A fuel oil additive as defined in claim **1**, said particles being 1 to 7 microns in size and the solids content of said dispersion being about 40 to 60% by weight.

3. A fuel oil additive as defined in claim **1**, said dispersion having a maximum Saybolt viscosity of 115 universal seconds at 80° F.

4. A fuel oil additive as defined in claim **1**, the elemental magnesium in said dispersion being greater than the amount of the elemental aluminum in said dispersion.

5. A fuel oil additive as defined in claim **1**, said petroleum oil having a maximum Saybolt viscosity of 35 universal seconds at 100° F.

6. A fuel oil additive as defined in claim **1**, said surfactant being present in the proportion of 0.7 to 3.5% by weight.

7. A fuel oil additive as defined in claim **1**, said surfactant being selected from the group consisting of glycerol stearates and laurates, lecithin, fatty acids, and heavy metal soaps of stearic, naphthenic and rosin acids.

8. A fuel oil additive as defined in claim **1**, said particles having a specific surface area of 400 to 1400 square meters per gram.

9. A fuel oil additive as defined in claim **1**, said particles being porous, the diameter of each pore in said particles being in the range of at least 17 angstrom units.

10. A fuel oil additive as defined in claim **1**, said particles being porous, the diameter of each pore in said particles being in the range of 17 to 20 angstrom units.

11. A fuel oil additive as defined in claim **1**, said particles having about 0.5 to 5% by weight of bound water.

12. A fuel oil additive as defined in claim **1**, the weight ratio of elemental magnesium:aluminum being about 10:1.

13. A method of preventing oil ash slagging, low temperature corrosion, acid smut emission, of reducing the level of SO_3 and nitrogen oxides in flue gases, chemically neutralizing and drying up gummy, corrosive deposits that form below acid dewpoint temperatures, in oil fired boilers comprising operating said boilers on a fuel oil containing about 1 gallon of additive in 1000 gallons of fuel oil to 1 gallon of additive in 2000 gallons of fuel oil, an additive comprising a petroleum oil having dispersed therein in the presence of an anionic or non-ionic surfactant 40 to 60% by weight of 1 to 7 micron particles of partially dehydrated hydroxides of Mg and Al having a minimum bound water content of about 0.5% by weight and a maximum bound water content of about 15% by weight, the weight ratio of magnesium:aluminum being at least 1:1.

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