

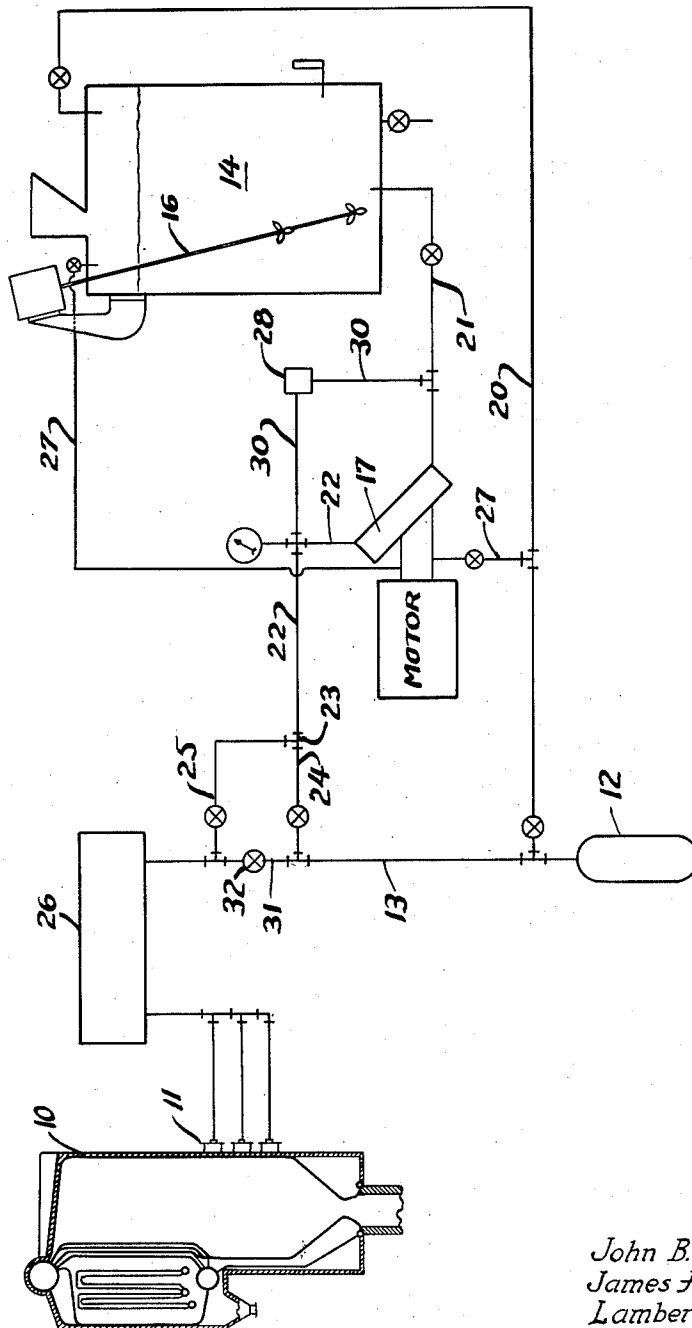
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ADDITIVES TO FUEL

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ADDITIVES TO FUEL

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The present invention relates to the suspension burning of ash-bearing fuels, and more particularly to the combustion of ash-bearing fuels in connection with the heating of tubular heat absorbing apparatus whereby the character of ash accumulation on the heat absorbing apparatus is modified by the addition of metal base materials.

When gaseous, liquid, or fine solid fuels are burned in suspension in the air supplied for combustion purposes the large proportion, if not the major portion, of the non-combustible constituents of the fuel are carried out of the furnace with the products of combustion. Efficient combustion of any of these fuels results in high temperatures, above the ash fusion temperature of at least the majority of the non-combustible ash constituents, so that suspended ash particles existing in the products of combustion will remain some time in a molten condition. While some cooling of the gaseous products of combustion and the suspended ash particles may result from furnace wall cooling, the ash particles are frequently at or above the temperature at which they are viscous when they leave the furnace and some attach themselves to tubular heat exchange surfaces extending across the gas stream. When superheaters for relatively high steam temperatures are involved, the metal temperature of the superheater tubes will be considerably higher than the metal temperature of the steam generating tubes. With the customary temperature of gases flowing over the superheater tubes a condition occurs which is conducive to the accumulation of slag or fused ash on such superheater tubes.

The accumulation of ash or slag on the heat exchange surfaces reduces the heat absorbing ability thereof and continued accumulation of slag will tend to build across the intertube spaces so as to increase the gas flow resistance, resulting in a reduction in the vapor generating and superheating capacity of the unit. While it has been the customary practice to periodically remove or reduce slag accumulations on the tubes by means of steam or water lances, or air blowers, it has been found in the suspension burning of some fuels the slag accumulation on the tubes is of such a tenacious character that the customary methods of slag removal are inadequate.

The quality of the liquid petroleum fuels burned in central station vapor generating plants has deteriorated during the past decade, particularly with regard to the amount and composition of the non-combustible constituents of the fuel. This not only results in an increasing amount of slag, but the nature of such slag has also changed so as to form hard rock-like deposits on the heat absorbing surfaces of the vapor generator. Apparently the slag is hardest and most difficult to remove by mechanical means when it has accumulated on relatively high temperature heat transfer surfaces, such as on the superheater tubes when a convection type steam superheater is arranged to deliver the steam at a temperature of the order of 800–1000 F., or higher. Samples of the hard, closely packed layers of slag deposited on the superheater tubes of generator units which have encountered slag difficulties have shown high vanadium and/or sodium

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sulfate contents. While such slags are somewhat corrosive in contact with the tubes the principal difficulty caused by the slag accumulations has been the reduction in the heat transfer rate to the fluid confined by the tubes.

5 Tube metal corrosion can occur by reason of these slag deposits with the seriousness of the corrosion problem increasing with increases in tube temperatures which promotes the formation of corrosive materials in contact with the tubes.

10 In the present invention metallic oxides having a relatively high melting temperature are combined with the slag forming constituents of the ash-bearing fuel to dilute and thereby modify the character of the slag whenever deposits are formed on the heat transfer surfaces of a vapor generating and superheating unit. This change in the character of the deposits is evidenced in that the physical nature is such that it is softer and more friable. While some chemical reactions between the residual elements from the fuel and the additives undoubtedly occur, the change as regards the deposits is considered to be primarily due to their diluent action in providing a matrix which makes the deposit more friable. With the use of additives it has become possible to maintain heat exchange surfaces clean over extended periods of operation without substantial loss of heat transfer efficiency, and with a minimum expenditure of slag removal labor costs.

In general this invention can be used in the suspension burning of ash-bearing fuel where it is desirable to increase the average fusion temperature of the non-combustible residue resulting from the combustion of the fuel. The invention is particularly advantageous in the burning of liquid petroleum fuels which form slags having high vanadium compounds and/or sodium sulfate contents.

15 According to the present invention the additive material is introduced into the combustion zone of the furnace so that finely divided high fusion temperature residual particles are dispersed through the gaseous products of combustion of the fuel and will be carried in suspension therein. More specifically the additive particles consist substantially of metallic oxides having fusion temperatures in excess of 2500 F. The additives may be introduced into the furnace in solution or suspension in the fuel; entrained with the combustion air; or injected separately at some other location in the furnace or boiler unit. This mixing of the additive material with the non-combustible ash constituents of the fuel is necessary for adequate dilution of the slag deposits. When using a liquid petroleum fuel, we prefer to mix the additive with the fuel prior to its combustion.

20 The additive may be metallic, aluminum or magnesium, which will be converted to the oxide under the combustion conditions in the furnace. Alternately, the additives may be in the form of an oxide of a metal such as for example MgO or CaO. When the additives are in the metallic oxide form, they can be a fine powder which may be mixed with the fuel or introduced for entrainment with the combustion air. As a further alternative, the additives may be in the form of an organic or inorganic compound of one of the metals aluminum, calcium or magnesium or as a natural or artificial combination of two or more of these metals, such as for example, salts of carboxylic acids or phenolic compounds or as metallic carbonates or hydrates.

25 Regardless of the original form of the additive, the non-combustible residues thereof must be in a non-reactive or inert form, i. e. substantially all of the oxides should be of aluminum, magnesium and/or calcium, with a minimized deposit of other metallic oxides, such as, for example, iron oxides and/or vanadium oxides, which have a catalytic effect as regards the formation of sulphur

trioxide and sodium-sulphur compounds under combustion temperature conditions.

In selecting an additive for use in any particular unit they should advantageously be of a low unit cost to minimize increases in the operating expenses of the heat exchange unit. However, in power generating units, where additives are used, the resulting ability to maintain clean heating surfaces over long periods of operation with low labor costs resulting from the changed characteristics of the slag deposits, will justify a reasonable additive expense.

As a general rule the amount of additive used is controlled so that the metal oxide slag diluent is approximately proportional to the weight of ash in the liquid fuel. This proportion will change with circumstances; as for example when a vapor generating unit is operated with a relatively high superheated steam temperature, the ratio of additive weight to fuel ash weight may require the formation of as much as two pounds of metal oxide for each pound of ash in the fuel. On the other hand, the ratio of additive weight to ash weight may be less than one when lower design superheat temperatures are involved in the vapor generator. The composition of the fuel ash will also influence the amount of additive material used.

By way of example, but not of limitation, a steam generating and superheating unit having a capacity of 300,000 pounds of steam per hour and a superheated steam temperature of 910 F. was fired with commercial fuel oil over extended periods of time, both with and without the use of a fuel additive. The fuel burned was No. 6 fuel oil ASTM designation D396-48T, with an average analysis of 3.0% sulphur and .12% ash, and having combustible constituents in excess of 99.0%.

When operating the unit without a fuel additive, the unit was removed from service twice each year for cleaning. A month or six weeks after each cleaning outage, it became necessary to lance the superheater with boiler water and to air lance and water wash the air heater. In addition, normal soot blower practice including automatic blowers in the superheater cavity between the wide and close spaced superheater tube banks, was continued.

An additive of the type described, in an amount substantially equal in weight to the ash content of the fuel, was used for extended operating periods for comparative purposes. Additives having a fineness of approximately 98% through the 325 mesh screen were mixed with the fuel oil prior to the introduction of the mixture into the furnace, through an atomizing burner.

The drawing illustrates a schematic arrangement of apparatus for carrying out the method of the present invention.

As shown, a vapor generator 10 of known type, as shown in detail by U. S. Patent No. 2,561,875, is fired by liquid petroleum fuel through the burners 11. The burners are positioned in a wall of the vapor generator to receive fuel under pressure from storage 12 through a supply conduit 13. A slurry of the liquid fuel and additive material is prepared in associated equipment which is connected with the conduit 13 for the removal of fuel therefrom and the introduction thereto of the slurry.

The arrangement of equipment for preparing a slurry of fuel oil and additive material, and mixing the slurry with the fuel oil delivered to the burners is illustrated in the drawing. As shown, the equipment includes a tank 14 having a usable capacity of approximately 250 gal. of slurry. The tank is provided with an external layer of heat insulating material, and is further provided with a motor driven agitator 16 to maintain the additive in liquid suspension while in the mixing tank. A motor driven slurry pump 17 is located externally of the mixing tank. The pump is arranged for variable speed operation and is interconnected with the tank 14 and the

burner fuel line 13 for the delivery of controlled amounts of additive containing slurry to the fuel burners 11.

Fuel oil for batch mixing with the additive is supplied through a valved pipe 20, while the slurry is withdrawn from the tank 14 through a pipe 21 leading to the inlet of the proportioning pump 17. The slurry discharge from the pump passes through a pipe 22 to a mixing T 23 where it mixes with the fuel oil moving through a stub connection 24 from the main fuel oil supply pipe 13. Leaving the T 23, the mixture of oil and slurry passes through a pipe 25 to the main supply pipe 13 and thence through a pressure regulating and flow metering station 26 to the burners 11. The pump 17 is of the flooded suction type, with a small sized tubular connection 27 leading from the pipe 20 to the pump and thence to the tank 14. A pressure relief valve 28 and connecting piping 30 between the discharge and inlet pipe connection is provided from and to the pump. Advantageously a by-pass pipe 31 and valve 32 connects the main supply pipe 13 section between the pipes 24 and 25, so that when necessary the additive supply to the burner can be discontinued without interruption of the fuel supply to the burners.

The use of the additive changed the characteristic of the slag deposits on the superheater tubes so that it was unnecessary to water wash or water lance the tube banks in order to remove some of the slag deposit. The customary use of steam soot blowing equipment was discontinued and it was found that adequate cleaning of the tube surfaces could be attained by air lancing with an air pressure of 225 p. s. i. The air lancing was done once a week and the unit was maintained in service with permissible reduction in heat transfer efficiency throughout the normal operating period of 6 months between shutdowns. The use of additives sometimes results in an increase in the rate of slag accumulation on the water tube walls of the furnace, but this slag can also be easily removed by the use of an air lance, when deemed desirable.

A comparison of the chemical analysis of the two deposits with and without alumina as the additive is tabulated below.

Chemical Analysis	Prior to Additives		With Additives	
	Percent		Percent	
SiO ₂	2.8		1.1	
Al ₂ O ₃	2.1		53.7	
TiO ₂	0.1		0.1	
Fe ₂ O ₃	1.8		3.2	
P ₂ O ₅	1.4		0.3	
P ₂ O ₆	0.037		0.06	
MnO.....	Nil		Nil	
CaO.....	7.8		2.4	
MgO.....	1.8		1.0	
SO ₃	43.8		18.6	
V ₂ O ₅	8.6		6.6	
NiO.....	2.9		1.3	
K ₂ O.....	8.6		1.2	
Na ₂ O.....	18.6		8.4	
Loss on ignition at 900° F.....	0.2		0.4	
Undetermined.....	Nil		1.7	
Total.....	100.5		100.0	
Fusion Temperatures	Red ¹		Oxid ²	
	Red	Oxid	Red	Oxid
Initial Def.....	2,260	1,640	2,900+	2,900+
Soft Temp.....	2,380	2,660	2,900+	2,900+
Fluid Temp.....	2,460	2,900+	2,900+	2,900+

¹ Shrinkage and drainage began at 1750 F. and continued through run.

² Shrinkage and drainage began at approximately 2050 F.

It will be noted that the addition of the additive to the petroleum fuel increased the Al₂O₃ content of the slag deposit to a value approximating 50% of the total, as might be expected, while the other chemical constituents of the slag are not changed proportionately. This may be caused by chemical changes in the slag, or by changes in the composition of the slag passing through the superheater bank and depositing on other

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surfaces in the unit or escaping with the gases of combustion.

The difference in the physical appearance of the slag samples was striking. The slag removed from the superheater tubes, after operation without the use of an additive, was hard and dense having a semi-fused rock-like appearance while the slag sample obtained after the use of the additive was granular, soft and powdery in appearance.

While in accordance with the provisions of the statutes we have illustrated and described herein a preferred embodiment of the invention, those skilled in the art will understand that changes may be made in the method of operation and form of the apparatus disclosed without departing from the spirit of the invention covered by our claims, and that certain features of the invention may sometimes be used to advantage without a corresponding use of other features.

We claim:

1. The method of burning an ash-bearing petroleum fuel oil in a combustion zone which comprises supplying a stream of said petroleum fuel oil to said combustion zone; withdrawing a small quantity of said fuel oil from the stream passing to said combustion zone; mixing said withdrawn fuel oil and a finely divided additive to form a slurry wherein said additive consists of a metal compound containing at least one of the metals aluminum, magnesium and calcium; mechanically agitating said slurry to maintain said finely divided additive in oil suspension; and adding a controlled quantity of said slurry to the fuel oil stream delivered to said combustion zone, said slurry being added at a rate sufficient to provide and additive weight addition to the fuel oil delivered to said combustion zone substantially equal to the weight of natural ash in the fuel oil.

2. Apparatus for preparing and burning an ash-bearing

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ing petroleum fuel oil which comprises walls defining a combustion chamber; a source of petroleum fuel oil; means connecting said source and said combustion chamber for fuel oil flow to the latter; tank means; means for withdrawing a small quantity of said fuel oil from said connecting means and discharging the oil to said tank means; means for introducing a finely divided additive to said tank to form a slurry wherein said additive consists of a metal compound containing at least one of the metals aluminum, magnesium and calcium; means for mechanically agitating said slurry to maintain said finely divided additive in oil suspension; a pipe connecting said tank to said fuel oil flow means for adding a controlled stream of said slurry to the fuel oil delivered to said combustion chamber; and proportioning pump means arranged to deliver said slurry to said fuel flow means from said tank at a rate sufficient to provide an additive weight addition to the fuel oil delivered to said combustion chamber substantially equal to the weight of natural ash in the fuel oil.

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