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ACTIVATED MANGANESE CONTAINING ADDITIVE FOR FUELS

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ABSTRACT OF THE DISCLOSURE

An activated manganese containing additive composition for fuels for retarding the corrosiveness of the ash and the ash slag buildup of such fuels upon combustion, such fuels including vanadium containing fuels and alkali, sulfur and iron containing coals. The said additive composition comprises a preparation of a manganese compound preferably and a metal salt of an alkyl-aryl sulfonate brought to a particle size in the range of 0.25 to 20 microns.

It is a prime object of the present invention to provide a specially activated manganese-containing fuel additive to retard the corrosiveness and the slag buildup of those residual fuels which contain such an amount of vanadium as normally to yield a corrosive and ash depositing vanadium-containing slag upon combustion.

It is a further object of this invention to provide such a fuel additive to render noncorrosive and nonslagging those residual fuels and coals which contain such an amount of alkali metal, iron or/and sulfur as normally to yield a corrosive, deposit-forming, adhering slag forming ash on the furnace tubes and walls upon combustion.

The activated manganese-containing additive of the invention is to be used generally with heavy fuel oils referred to in the trade as #4, #5 and/or #6 oil, the latter commonly called Bunker C fuel. It may be used also with crude oil, as well as any other fuel of a liquid nature including distillate fuels, in order to improve the burning properties of the fuel and, where applicable, to prevent the buildup of either hard slag or carbon deposits. The additive preparation can likewise be used with coals, as well as petroleum cokes.

It has been observed that when a residual type fuel oil containing substantial amounts of vanadium is burned in furnaces, boilers and gas turbines, the ash resulting from combustion of the fuel oil is highly corrosive to materials of construction at elevated temperatures and attacks such parts as boiler tubes, hangers, turbine blades, and the like. These effects are particularly noticeable in gas turbines. Aside from corrosion, the formation of deposits upon the burning of a residual fuel in a gas turbine may result in unbalance of the turbine blades, clogging of openings and reducing thermal efficiency of the turbine.

Substantially identical problems are encountered when using a solid residual petroleum fuel containing substantial amounts of vanadium. These fuels are petroleum residues obtained by known methods of petroleum refining such as deep vacuum reduction of asphaltic crudes to obtain solid residues, visbreaking of liquid distillation bottoms followed by distillation to obtain solid residues, coking of liquid distillation bottoms, and the like. The solid residues thus obtained are known variously as petroleum pitches or cokes and find use as fuels. Since the vanadium content of the original crude oil tends to concentrate in the residual fractions, and since the processing of the residual fractions to solid residues results in further concentration of the vanadium in the solid residues, the vanadium corrosion problem tends to be intensified in using the solid residues as fuel.

The vanadium-containing ash present in the hot flue gas obtained from the burning of a residual fuel containing substantial amounts of vanadium compounds causes "catastrophic" corrosion of the turbine blades and other metal parts in a gas turbine. The corrosive nature of the ash appears to be due to its vanadium oxide content. Certain inorganic compounds of vanadium, such as vanadium oxide (V_2O_5), which are formed on combustion of a residual fuel oil containing vanadium compounds, vigorously attack various metals, their alloys, and other materials at the elevated temperatures encountered in the combustion gases, the rate of attack becoming progressively more severe as the temperature is increased. The vanadium-containing ash forms deposits on the parts affected and corrosively reacts with them. It is a hard, adherent material when cooled to ordinary temperatures.

It is to be noted that the corrosion of materials at high temperatures by the hot ash resulting from the combustion of a vanadium-containing residual fuel is to be distinguished from the type of corrosion occurring at atmospheric or slightly elevated temperatures, generally in the presence of air and moisture. Under the latter conditions, as ash containing vanadium oxide has no directly significant corrosive effect. The corrosion problem described herein may therefore properly be termed a problem of "hot corrosion."

The economic factors involved preclude any extensive treatment of vanadium-containing residual fuels to remove the vanadium therefrom or to mitigate its effects. The vanadium compounds in residual oils are not removed by centrifuging or by the conventional chemical refining treatments.

It has been disclosed that oil-soluble manganese-containing salts, particularly of the fatty acid types, are effective for rendering noncorrosive fuels that contain vanadium, sodium and sulfur only when used in substantial quantities in a fuel oil, generally when employed in an amount sufficient to give an identical atom ratio of metal to the vanadium of 6:1, generally not less than an atom ratio of 3:1, and certainly no less than 2:1. Moreover, even at the higher ratios of 4:1 or even 6:1, the oil-soluble manganese soaps of the fatty acids, of the sulfonates, or the like do not reduce the adherence characteristics of the deposits to the metal tubes. This likewise is the case when manganese oxides, hydroxides, carbonates and similar basic salts are by themselves, or in combinations of the above, added to a fuel-fired furnace, or when the manganese oxides in a kerosene-slurry is added to the vanadium containing fuels.

As illustrative of the surprising characteristics of the product of this invention, I have discovered that when I treat a manganese oxide with a specific amount of an oil-soluble metal salt, preferably a barium salt of an alkyl-aryl sulfonate derived from a sulfonic acid of 375 to 500 average molecular weight and the final manganese preparation is brought to a particle size preferably in the range of 0.5 to 5 microns, then unexpectedly and unpredictably, the vanadium-containing fuels are rendered noncorrosive and nondepositing even when employed at very low atom ratios of manganese to vanadium in the fuel oil of 0.25 to 1, or 0.5 to 1, in each case considerably lower than heretofore believed possible.

Where this additive preparation is used with diesel fuel, jet fuel, fuels for gas turbines, or even gasolines, the preparation is not added to the main fuel storage tank. This is one distinguishing feature of the invention because the product is not soluble in the light hydrocarbon range of distillate fuels, unlike the manganese tallates or other oil-soluble manganese compounds disclosed in the Ambrose Pat. No. 2,943,925 of July 5, 1960 and in the Brown et al. Pat. 2,818,416 of Dec. 31, 1967. Enhanced properties, particularly for preventing slags and deposits, are pro-

duced because of the discrete particle sizes of the additive preparation of this invention. To be effective, the manganese-containing preparation of this invention should be added to the diesel engine proper, to the combustor in the case of a gas turbine, or added concurrently with the fuel just before the fuel goes into the engine or the gas turbine. Similarly, with a furnace of any kind burning light distillate fuels, it can be added directly into the furnace box, injected into the rear end of the furnace or concurrently with the fuel that is either being atomized, sprayed or injected into the furnace box.

The manganese-containing preparations of this invention surprisingly function as smoke-reducing agents and as soot-destroying catalysts even when added to the fuels in surprisingly small quantities of 60–120 parts per million of manganese in the fuel oil, and as little as 10–20 parts per million. Because it frequently is important to render a fuel both nondepositing and non-sooting, it will be obvious to those versed in the art that only the manganese preparation of this invention can carry out both objectives simultaneously and which cannot be achieved by combining all other known manganese-containing additives.

I have also found that the manganese-containing preparation of this invention when used either as the liquid product containing 15–27 percent by weight of manganese, or as the solid product containing even as high as 70 percent manganese by weight when added to coals renders them noncorrosive and nondepositing even when the coals normally would be corrosive or depositing, such as occurs with coals that contain a high percentage of alkali, iron oxide or a ratio of base-forming ash oxides to that of acid-forming ash oxides that would result in ash deposits adhering to the furnace walls and tubes in the temperature regions of 1800 to 2300 degrees Fahrenheit. The manganese-containing preparations of this invention, I have discovered, will raise the ash-fusion points of low fusion point coals by a range of 100 to 500 degrees Fahrenheit, sufficient to render the coal ash nondepositing in those sections of the furnace that are in the critical, fusing, temperature zones of the furnace. Additive liquid preparations of this invention containing lesser amounts of manganese are, of course, possible. This, however, makes them less economical to use in a coal fired furnace.

The type of residual fuel oils to which my invention is directed is exemplified by No. 5, No. 6 and Bunker "C" fuel oils which contain a sufficient amount of vanadium to form a corrosive ash upon combustion. These are residual type fuel oils obtained from petroleum by methods known to the art. For example, residual fuel oils are obtained as liquid residua by the conventional distillation of total crudes, by atmospheric and vacuum reduction of total crudes, by the thermal cracking of topped crudes, by visbreaking heavy petroleum residue, and other conventional treatments of heavy petroleum oils. Residua thus obtained are sometimes diluted with distillate fuel oil stocks, known as "cutter" stocks, and the invention also includes residual fuel oils so obtained, provided that such oils contain sufficient vanadium normally to exhibit the corrosion characteristics described herein. It should be understood that distillate fuel oils themselves contain either no vanadium or such small amounts as to present no problem of hot corrosion. The total ash from commercial residual fuel oils usually ranges from about 0.02 to 0.2 percent by weight. The vanadium pentoxide (V_2O_5) content of such ashes ranges from zero to trace amounts up to about 5 percent by weight for low vanadium stocks, exhibiting no significant vanadium corrosion problem, to as much as 85 percent by weight for some of the high vanadium stocks, exhibiting severe corrosion.

The type of vanadium-containing solid residual fuels to which the invention is directed is exemplified by the coke obtained in known manner by the delayed thermal coking or fluidized coking of topped or reduced crude oils and by the pitches obtained in known manner by the deep vacuum reduction of asphaltic crudes to obtain solid res-

idues. These materials have ash contents of the order of 0.18 percent by weight, more or less, and contain corrosive amounts of vanadium when prepared from stocks containing substantial amounts of vanadium. A typical pitch exhibiting corrosive characteristics upon combustion had a softening point of 347° F. and a vanadium content, as vanadium, of 578 parts per million.

This invention is directed further to alkali-containing coals, iron-containing coals, sulfur containing coals as well as combinations of any two or three of the above elements. More particularly it is concerned with rendering noncorrosive and nonslagging those coals which contain an amount of alkali metal, iron and sulfur as normally to yield a corrosive or slag forming ash upon combustion.

This invention is also directed to sulfur containing petroleum fuels and sulfur containing coals and sulfur containing fuels in general that yield a toxic, corrosive or otherwise irritating oxides of sulfur upon combustion.

The use of manganese containing oil soluble or oil dispersible salts employed in amounts of additive as to result in at least 3 atoms weight of the manganese to the salt per atom weight of the vanadium in the fuel oil and preferably atom weight ratios of Mn:V of 6:1 or larger although not outside of the scope of this invention in terms of the atom weight ratios of manganese required have been found to be economically unjustified as a result of this invention. Moreover, at these high atom ratios of Mn:V, substantial ash deposits result.

Whereas large ratios of Mn:V, or particularly Mn:S may be required for air pollution control measures as further described in this invention or for certain very high combustion furnaces operating at temperatures in excess of 2,000° F. metal tube temperatures, or wall, or refractory wall surface temperatures, I find that to obtain corrective action for reducing slag, SO_3 in the flue gases, low temperature flue gas corrosion and elimination of smoke or soot representing unburned hydrocarbons that considerably lower weight ratios of manganese in the fuel are required than have hitherto been disclosed or economical. For example, complexes of manganese of zerovalence with chelating agents are expensive to begin with and further do not give the beneficial results possible with the low cost manganese-containing composition of this invention. I believe, but only by way of explanation, that when the manganese salt is present as a true oil soluble material of particle size less than 0.01 micron that the oxidized forms of the manganese upon combustion tend to form crystal growth patterns and agglomerated, large size, manganese containing-ash in the furnace that nullifies the corrective action of the manganese that would otherwise result from the use of same.

For exactly opposite reasons, the use of manganese oxides, manganese carbonates, manganese containing clays as ordinarily available as an article of commerce having generally particle sizes of 10 to 400 microns, or higher, are ineffective because of the low activity of these large particle sizes that make them unfavorable for reacting with the vanadiums, the sulfur oxides and in general the ash-comprising portions of the petroleum fuels or the coals. The quantity of such naturally occurring manganese required to bring about the effective control is too great for useful operations and would leave too much deposits behind in the furnace. Simply grinding down the manganese oxides by use of pulverizing mills or fluid energizing mills, by itself or in combination with kerosene-like solvents, or even polar-type solvents, is also ineffective for the purposes of boiler control because the manganese oxides tend to reaggregate or in any case do not show the surprising and dramatic results that are obtained with the manganese material as disclosed herein wherein the manganese particles apparently become coated with a protective layer as a result of the complex that is formed with the coagent of this invention.

Likewise, the use of salts of manganese which contain an acid portion derived from a sulfate, nitrate, acetate, or

chloride is ineffective because the manganese is unavailable to react in the furnace, engine or turbine with the sulfites, sulfates or sulfur oxides derived from the combustion process or with the vanadates or the iron sulfates, these latter materials being the object of this described invention whereby the reaction of the manganese herein destroys the corrosiveness of the slag depositing tendencies of these materials.

It has been unexpectedly observed that the slag forming tendencies of residual fuels, the slag forming tendencies of coals, the corrosion tendencies of vanadium containing fuels, as well as alkali and/or iron containing coals, the acidic sulfur oxide-forming tendencies of fuels and coals can be rendered noncorrosive and nonslagging by adding to the fuel or coal a sufficient quantity of manganese prepared by comixing preferably in a high energy type mill or a high-shear mixer, such as a Banbury mill, Cowles Dispersator, a Hockmeyer, a steel or porcelain ball mill, Morehouse or Premier colloid mill, or to an attritor such as a batch size or continuous ball mill, a sand mill or a pebble mill, or to a three-roll paint mill, the following charge:

A mixture of a manganese oxide with a minor amount of a barium salt of an alkyl aryl oil soluble sulfonic acid where the particle size of the combination is in the range of 0.5 to 10 microns, but preferably in the range of 1 to 5 microns, but also applicable being in the particle size of 0.25 to 20 microns.

Below a particle size of 0.1 micron, the combustion products from the manganese tend to crystallize in the furnace or engine resulting in an increase of the deposits in the furnace. Above a particle size of 40 microns, the manganese-containing particles are too inactive to carry out the requisite slag and corrosion inhibiting properties.

It further it necessary to make the manganese and co-agent in the manner described above in order to make a stable composition when adding solvents or oils to liquify said manganese oxides and also to prevent settling of the manganese oxides when added to a petroleum fuel.

It is not absolutely essential that the barium alkyl aryl salt be co-added with the manganese oxides before the grinding process. The manganese oxides can be prior ground to the proper particle size and then comixed under high speed shear with the barium coagent salt, in the form of a liquid composition, or in the form of a powder composition.

In each case above, generally the atomic weight ratio of manganese:barium in the final composition is 100:0.5, but could vary from 100:0.1 to 100:3.0.

The preferred starting manganese compounds for this invention are MnO , Mn_2O_3 , Mn_3O_4 or combinations thereof.

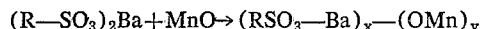
Although not necessary in describing the action of the manganese as shown in this invention from the preparation point of view, it is important to the understanding of this invention that the combustion process be understood. During the combustion process, the manganese-containing barium coadduct product is acted upon to form the active manganese material that is reactive with the slag forming and corrosion forming materials present in the fuel or coal as well as with the unburned soots or hydrocarbons present in the furnace or diesel.

If we further understand that the active manganese is formed in-situ in the furnace process and that the manganese regenerates itself, it would explain the low quantities of manganese that suffice to bring about reduction of corrosion, slagging and smoking.

It has been observed that when the manganese oxides mixed in a vehicle such as a petroleum oil having an API gravity of 26.0, a pour point of $-45^\circ F.$, a viscosity between 80 and 90 SSU at $100^\circ F.$ is admixed with the barium alkyl aryl sulfate of this invention there is a noticeable heat of reaction occurring. This shows that a new

complex has formed of Ba-alkyl-aryl-sulfonate: Mn_xO_y ; the exact composition has not been determined or analyzed further since it has been found that the activity is unattainable except as produced as described herein.

For illustrative purposes in contemplating the type of complex formation that might be occurring here, but not to be taken as limiting the invention or as a necessary part of this invention, I believe that the complex that occurs between the manganese oxide and the barium alkyl aryl sulfonate could be as shown below:



where R is the alkyl aryl group of 330 to 370 molecular weight, and x and y could each be 1, but y could be a multiple 2, 3, or 4 and x might also be 2 or 3. Indirect methods, such as determining the micelle molecular weight of the complex by colloidal dye-absorption methods indicate that the complex could have a molecular weight of 2,000 to 20,000, which would indicate an associative polymer where x and y would each be greater than 1.

Applicable but less desirable as the metal of the coagent salt of this invention are the cations of calcium, cadmium, magnesium, iron, zinc, sodium, potassium, lead, nickel, tin, aluminum, strontium, chromium, zirconium, manganese, cobalt, copper and ammonium or similar amine derived cations which can be substituted for the barium. When these other cation salts of alkyl aryl salts are comixed with the manganese oxides, there is a considerably lesser heat evolution which indicates that the complex co-adduct is not as stable nor is it as effective as with the barium. With the use of each of these metals, the atomic weight ratio of manganese to the metal in the final composition is fixed in the range of 100:0.1 to 100:3.0.

Similarly when the barium is the source of the cation it is found that other acidic organic compounds that form oil soluble salts with barium can be used, but again when comixed with the manganese oxide as in this invention considerably less heat of reactions are involved. Representative examples are: (1) the fatty acids of at least 5 carbon atoms, e.g., valeric, caproic, 2-ethylhexanoic, oleic, palmitic, stearic, linoleic, tall oil, and the like; (2) oil-soluble alkyl aryl sulfonic acids, e.g., oil-soluble petroleum sulfonic acids and dodecylbenzenesulfonic acid; (3) long chain alkylsulfuric acids, e.g., lauryl sulfuric acid; (4) petroleum naphthenic acids; (5) rosin and hydrogenated rosin; (6) alkyl phenols, e.g., iso-octyl phenol, t-butylphenol and the like; (7) alkylphenol sulfides, e.g., bis-(iso-octyl phenol) monosulfide, bis(t-butylphenol) disulfide, and the like; and (8) oil-soluble phenolformaldehyde resins, e.g., the Amberols, such as t-butylphenol-formaldehyde resin, and the like. Since the salts or soaps of such acidic organic compounds as the fatty acids, naphthenic acids and rosins are readily available or can easily be prepared, these are preferred materials. Particularly preferred are manganese naphthenate, manganese oleate, manganese tallate (tall oil soaps) and manganese rosinat.

Although manganese containing additives have in effect been suggested as fuel oil treatments in the past, we have found, quite unexpectedly, that when a product is made according to the disclosure contained herein, that an unusually effective material results, resulting in improved burning properties, reduced deposit-forming tendencies, clearer stacks and overall cleaner firesides.

The previous art has been known to use manganese additives generally in the form of a fatty acid soap, naphthenate, tallate, rosin-acid, linoleate, or in the form of so-called, "zerovalent coordinated complexes" which are defined by the fact that the manganese in this latter compound has a so-called zerovalent state, as an example of which is manganese cyclopentadienyl tricarbonyl, or other manganese salts which are in the form of acetyl acetonates or other chelated complexes. In either case, the manganese containing additives are relatively expensive and their utilization is accordingly limited by the high cost of treating fuels with such materials.

Other known forms of manganese preparations are its use in the form of a slurry in a solvent, or in some cases, in the form of an emulsion, or even as solid particles of various forms of manganese oxides.

Although the latter form of the manganese containing products are comparatively inexpensive, when added to a furnace, the manganese is found to be rather ineffective as a combustion improver or a slag inhibitor. We believe that the particle sizes are too large and that the catalytically active sites of the manganese are either nonpresent or not available for reacting with either the carbon particles in order to combust them or with the vanadium and sulfur-containing deposits in order to react with the latter and cause greater overall fireside cleanliness. In addition, the oil soluble manganese containing soaps and organic hydrocarbon complexes, in addition to being relatively expensive, also tend to produce large deposit aggregates in the furnace. These are difficult to remove and in many cases are even more troublesome than not treating the fuels in the first place. It is one object of this invention to activate the manganese particles so that they will be effective as combustion improvers.

We believe, although this is not necessarily binding to our disclosure, that the reason why the oil soluble manganese-containing additives build up into large clusters in the boiler is the result of crystal growth in the furnace. The extremely fine size manganese oxides, manganese vanadates, manganese sulfates, manganese vanadyl sulfates, sodium manganese vanadyl sulfates, and sodium manganese vanadates form poly-aggregates from the reaction of the manganese with the deposit-forming sodium, vanadium and sulfur products of combustion. The crystals tend to grow and leave behind on the furnace tubes and walls these big clusters that subsequently tend to adhere to the fireside tubes making cleaning that much more difficult.

In the present invention, we find that the manganese containing additive is not only effective for eliminating carbon buildup as well as ash deposits, but large crystal growth does not occur. As a result, the furnaces are left clean with only a light, fine and easily removed tan powder, the latter being the high melting complexes of the manganese with the ash from the fuel. This fine powder is easily eliminated either during the routine use of soot blowing or by the natural draft in the furnace.

I believe that the reason for the unexpected results obtained with the product of the present invention is a function of the method of preparation which tends to activate each manganese particle, as well as the controlled particle size of the manganese containing additive. I believe that each active manganese particle becomes coated with the surfactant particle as employed in this invention, which, in turn, stabilizes the manganese. This will be illustrated in the following example.

In a typical preparation of this invention, selective manganese oxides are broken down in particle size and reacted with a surface active agent preferably one containing a divalent metal salt. Generally the surfactant is added before the grinding and aids in the grinding process. The manganese oxides form a new, hitherto undisclosed, complex with the divalent metal-containing surfactant of this invention. This complexing process has the effect of activating the manganese oxide and keeping it in a small particle size and in a dispersed phase so that it has instantaneous ability to react in the furnace either with the unburned carbon or with the ash-containing impurities in the fuel or coal. The combination of the grinding technique with the divalent surfactant used in the preparation keeps the particle size of our product in the range of 0.1 to 40 microns in the widest latitude, but generally in the range of 1 to 5 microns. Within this broader or specific particle size region, it was found in practice that an extraordinary degree of fireside improvement is obtained that does not result with either with the completely oil-soluble materials

or with the coarser slurries of unstable mixtures of manganese oxides in solvents, in water-slurries, or in emulsions.

More specifically, one takes raw manganese oxide and grinds this in one of several types of grinding equipment, including the use of a ball mill, to a particle size of less than 10 microns, and preferably below 5 microns. To this fine manganese oxide powder, one adds a carrier oil or solvent which then is mixed with a surfactant such as an oil-soluble barium aryl-alkyl sulfonate and the entire mixture is then reground in a high speed shearing apparatus, including the use of a ball mill. That a complex is formed is evidenced by an enormous heat of reaction that occurs when the barium sulfonate reacts chemically with the finely ground manganese oxide. The exact nature of this complex is not known, but the product shows unusually good stability when tested by any sedimentation method, which otherwise would tend to cause rapid sedimentation of the manganese oxides from a slurry, or from a metastable combination due to the coarser particles of discrete manganese oxides settling out.

The surfactant may be any substances known to have such properties. Particularly effective are the ammonium, amine, hydroxyl amine, quaternary amine, calcium, magnesium, sodium, potassium, strontium, beryllium, zinc or barium salts of (a) tall oil fatty acid, naphthenic acids, octoic or 2-ethylhexoic acids, long chain or oil-soluble carboxylic (fatty) acids of natural or synthetic origin; (b) sulfonic acids of petroleum or synthetic origin; (c) oil-soluble alkyl phenols, as well as organic phosphorous compounds, phosphorous-sulphide treated olefins, non-ionic oil soluble surfactants and cationic oil-soluble surfactants.

The preferred sulfonate for use in this invention, both because of its molecular weight, configuration, proven suitability, as well as its availability and low cost, and accordingly the preferred material, would be derived from so-called "bottoms" obtained during the sulfonation with SO_3 , oleum, or sulfuric acid of petroleum refinery hydrocarbons, generally high in aromatic content, which results materially in a water-soluble alkyl aryl sulfonate (as the sodium salt) with a molecular weight generally below 300 (as sodium salt), whereas the "by-product" bottoms would have a molecular weight of generally between 350 to 510 as the sodium salt. The main criterion in this invention is that the alkyl aryl sulfonates obtained from these bottoms are oil soluble (as their sodium salts). These sodium aryl-alkyl sulfonates are then converted by simple metathesis, generally with barium chloride to the corresponding barium salt, which is the preferred coagent of this invention. The molecular weight of the coagent containing barium as the cation would have a preferred molecular weight of approximately 1000 when derived from the corresponding sodium salt which has a preferred molecular weight of 440 to 450.

To those skilled in the art of sulfonation, other methods of preparing alkyl aryl sulfonates will be apparent. Further for the purpose of use as a coagent, it is possible to use a metallic salt of a sulfonated aromatic (mono-, di-, tri- or multi-aromatic) or the sulfonate of a paraffinic or naphthenic hydrocarbon, and, in the latter case, with or without an aromatic ring, with the main criterion being that the metallic salt of the sulfonated hydrocarbon should be soluble in a petroleum oil, or, as referred to in the trade, as "oil-soluble." The preparation of the preferred hydrocarbon feedstock for sulfonation to an oil soluble product by alkylation or other techniques is well known in the art.

The same is correspondingly true for the alkyl aryl sulfonates that would correspondingly be converted into calcium or other metallic salts that are useful as coagents in this invention. The molecular weight, the size and the polarity of the barium cation could explain why the barium alkyl-aryl sulfonate is the preferred coagent for this invention since it may form the strongest coordinated

bonds when complexed with the manganese oxides of this invention, but this is not to be construed as limiting the scope of this invention. It is a significant part of this invention, for example, that the manganese salt of the alkyl aryl sulfonates likewise complex with the manganese oxides and the resultant complex is a desirable and benefitting fuel and coal improving agent.

By this process, it is possible to make a fuel treatment containing typically 25-27% manganese by weight, where the final preparation is still free-flowing can be stored for extended periods, even in cold climates.

Other dispersing additives for the manganese oxide can be used such as calcium alkyl-aryl sulfonates or the salts of calcium or barium with tall oil fatty acids, naphthenic acids, or long chain carboxylic acids that result in an oil soluble metal salt as the coadduct portion of this invention.

The source of the manganese can be either manganous oxide or hydroxide, manganic hydroxide or oxide, and even manganous or manganic carbonate, or mixed salts of the above.

TEST METHODS

In order to demonstrate and evaluate the effectiveness of the manganese-containing product of this invention, various tests have been employed as described below:

Slag-inhibiting test

An equal weight of a synthetically prepared slag which is primarily composed of sodium vanadyl sulfates and the manganese containing product of this invention is mixed and then placed in a muffle furnace at a temperature of 1275° F. for a period of 24 hours. The untreated sodium vanadyl sulfate serves as a control. After the stainless steel dishes, in which the preparations are contained, are cooled to room temperature, the resultant deposits then are examined for hardness, adhesion to the stainless steel dish and friability characteristics.

Soot ignition test

Lampblack, or furnace soot, is mixed with the manganese-containing preparation of this invention in the ratio of 1 gram soot and 0.04 gram of additive. The mixture contained in a porcelain capsule is ignited and the dishes then are placed in a muffle furnace at 900° F. for a period of two hours. The untreated sample of lampblack serves as a control. The amount of soot burnoff then is determined by weighing the residue or by determining the degree of whiteness of the crucible which is an indication of the amount of burnoff.

Diesel combustion test

The #2 fuel oil, or a diesel oil, is treated with the manganese-containing preparation of this invention in sufficient quantities to supply the particular amount of manganese as described in the test procedures. Then, 2 cc. of the treated fuel is flared off in the porcelain dish and the resultant residue then is placed in a muffle furnace maintained at a temperature of 800° F. for a period of two hours. As a control, a sample of untreated #2 oil or diesel fuel is ignited and likewise placed in the muffle furnace. The improvement in the combustion as a result of the chemical additive is noted by the degree of whiteness that results after the heating cycle.

Fuel oil combustion efficiency test

The manganese-containing composition of this invention, sufficient to supply 15 parts per million of manganese to a fuel oil having a viscosity of 2000 Redwood seconds at 100° F., an ash of 0.01 percent by weight, a vanadium content of 10 parts per million, a sodium content of 10 parts per million and 1.4% sulfur is placed in a porcelain dish containing 2 cc. of the above-treated fuel oil and the dish is heated until the fire temperature of the oil is reached and the oil ignites. After the oil has burned itself out, the dish containing the residue from the ignition is

placed in a muffle furnace and heated for 2 hours at 950° F. At the end of this time, the dish is removed and the extent of unburned material, as noted by the percent whiteness of the dish is determined by inspection. An identical fuel oil without the manganese-containing composition of this invention is run for purposes of comparison.

Fuel-ash test

The manganese-preparation of this invention is placed in a 4" diameter 18-8 stainless steel dish and the dish is heated until the fire temperature of the oil is reached and the oil ignites. After the oil has burned itself out, the dish containing the residue from the ignition is placed in a muffle furnace and heated for 8 hours at 1350° F. At the end of this time, the dish is allowed to cool slowly and the nature of the ash is determined by inspection. An identical residual fuel oil without the manganese preparation is run for purposes of comparison. The nature of the ashes left behind with the treated and untreated fuels then are examined for hardness, fusion temperatures and adherency to the stainless steel dishes, or for any signs of corrosion.

Accelerated gas turbine corrosion, slag and combustion test

The procedure in use is similar to that employed by Ambrose in his aforesaid patent with the following changes. The fuel is aspirated through the hypodermic needle rather than being pumped to insure uniform addition of fuel and additive. The test is run for a period of 8 hours, rather than 100 hours; the temperatures are varied from 1000° to 2000° F. to get broader results under different test temperatures; also the combustion bases are passed through scrubbers to determine sulfur dioxide, sulfur trioxide, nitrogen oxides and particulates in the exhaust gases.

In-plant trial

A pressurized furnace operating at 1050° F. superheat and reheat temperatures, a furnace pressure of 2000 p.s.i.g., steam atomized fuel was operated for a period of 4 months with the residual fuel that was burned having been treated continuously with the manganese-containing composition of this invention sufficient to supply 70 parts per million manganese to the fuel which contained 0.035 percent ash, an average of 85 parts vanadium and 1.0 percent sulfur. An identical twin furnace burning the identical residual fuel oil without the manganese-containing composition of this invention was run for the identical period of time for purposes of comparison.

A magnesium-containing additive or preparation when added to a vanadium-containing fuel has been known to prevent corrosion, as well as deposit buildup on metal tubes subjected to temperatures of 950° F. and higher, as occurs in gas turbines and on fireside furnace tubes and wall samples that typically burn an ash-containing residual fuel. This magnesium preparation can be one as defined in my prior Pat. No. 3,332,755 or it can be a mere slurry of magnesium oxide or magnesium hydroxide in oil or solvent. Although these magnesium compounds, even the slurried form, may bind up the vanadates and sulfates that form in the furnace, they tend to deposit magnesium vanadates or magnesium sulfates or magnesium vanadyl sulfates in the furnace.

A novelty of the present invention is that one can periodically add the manganese-containing preparation of this invention to furnace or to the fuel that is being treated on a continuous basis with the magnesium compounds. The net effect is to loosen the magnesium complexes that form on the furnace, resulting in a cleaner furnace.

In other words, the manganese preparation as defined herein is extremely effective for eliminating complex magnesium salts derived from the magnesium and the inorganic ash constituents of the fuel that may have a tendency to build up on the furnace tubes or walls.

In other words, in this dual treating system, the magnesium materials are used to complex the ash forming impurities present in the fuel or in the coals; these complexes are then removed from the tubes by the less frequent, or intermittent use of the manganese additive of this invention, either added to the fuel oil or injected into the furnace proper.

This, in effect, serves a unique or dual purpose in that the vanadium or sulfate deposits are kept from adhering to the tubes, and at the same time keeping the furnaces clean, often to bare metal. Since magnesium does not have any combustion properties, the introduction of the manganese additive of this invention has the overall effect of improving the combustion of the fuel by its property of burning off carbon at lower furnace temperatures and at the same time eliminating the magnesium deposits that form from the prior use of the magnesium-containing constituents.

It should be noted that one ordinarily would not comix the magnesium with the manganese in suitable proportions, such as defined in this invention, since the introduction of the manganese often tends to destroy the slag reducing properties of the magnesium, and vice versa, presumably because a magnesium manganate salt forms in-situ which destroys the activity of the manganese and the magnesium as slag-retarding materials. This can be demonstrated by means of the Slag Test described in this application, whereby it is shown that a magnesium-containing preparation by itself forms a more friable ash when reacted with the sodium vanadyl sulfate than occurs with a mixture of magnesium with manganese.

One can, however, substitute silica for magnesium by adding a finely ground silica, either as a powder or as a slurry, or in some way that causes the fuel to be burned concurrently with the addition of the silica with the concurrent addition of the manganese. In this specific case, the silica and the manganese can be added together in the additive preparation. The fuel containing the silica does not result in the buildup of hard, corrosive or adhering slag on the furnace walls or tubes when the fuels contain appreciable quantities of vanadium in the case of petroleum-derived residual fuels or pitches from the deep vacuum reduction of asphaltic crudes, or appreciable quantities of alkali and/or iron, in the case of solid coals. In this instance, the manganese of this invention can be added separately to the fuel, to the coal, or to the furnace on a continuous or on a continual or intermittent basis, or the manganese of this invention can be mixed together with the silica and the whole added to the fuel, the coal, or the furnace, which in this case is possible, presumably because the manganese does not form a reaction product with the silica, when present in the small amounts required herein and accordingly the manganese of this invention acts to keep the furnace walls and tubes from accumulating a buildup of voluminous or extensive ash that represents the mixture or end-product of the combination of the silica with the inorganic constituents of the fuel. That this is possible is further demonstrated by mixing silica with the manganese preparation of this invention together in a ratio to supply by weights 9 parts silica with 0.5 to 3 parts of manganese, mixing this combination intimately with an equal part by weight of a fuel oil ash derived from a vanadium-containing residual fuel and maintaining the mixture in a 25-20 stainless steel dish for 24 hours at 1450° F., then removing the dish for observation and comparison with the identical fuel oil ash maintained under identical conditions. The untreated ash is found to be dense, hard and adheres to the dish, whereas the treated ash is powdery, loose, and easily crushed.

It has also been possible to carry out the teachings of this invention by continuously treating the residual fuel containing vanadium with the manganese of this invention to supply 10 to 120 parts per million manganese and intermittently add to the fuel oil or the furnace inorganic oxides that are known to prevent vanadium deposits from

forming dense and hard deposits, such materials being typically magnesium oxide, magnesium hydroxide, dolomites, silica, kaolins, aluminas, montmorillonite, pyrophyllite or the like, added as a powder, a slurry or as an emulsion to the fuel or the furnace. The amount of inorganic oxide is not a critical factor when used in this manner with the fuel being treated with the manganese of this invention, which is the really effective chemically reactive agent, whereas the above referred-to oxides or salts apparently physically adsorb the vanadium-containing ash and somehow prevent the latter from forming the densely adhering deposits that would otherwise form hard crusts on the tubes, but at the penalty of greatly increasing the total ash in the fuel or furnace, since, and quite obviously, a chemical reaction does not occur to a major degree, but rather a physical adsorption. The manganese of this invention apparently prevents the large buildup of the physically-combined ash in a manner that is not entirely or clearly understood. Generally, but not to be construed as limiting in this example, the magnesium oxide or silica or other inorganic oxide referred to above should be added to the fuel at a rate to supply on an overall basis 0.005 percent by weight to 0.25 percent by weight.

Likewise, when referring to an alkali and/or iron-containing coal, the manganese of this invention can be added to the coal in combination with the magnesium oxides or hydroxides, silica, dolomite, and the other referred-to inorganic clays under precisely the same conditions as disclosed for the fuel oils within the same limitations as shown. Preferably, with coals the magnesites and the dolomite types of inorganic adsorbing agent is preferred, since most coals already contain appreciable quantities of silica and alumina, so that the additional introduction of silica or alumina or acid-type oxides show less improvement over the basic-oxides. The use of dolomite as an adduct to coals or fuels as an air pollution correction measure to react with SO₂ to form a sulfate has been found to be dramatically improved by the coaddition of small amounts of my manganese-containing invention added to the fuel or coal, or to the furnace, or mixing the manganese product with the dolomite. By so doing the quantities of dolomite required to react with the SO₂ is reduced considerably because of the activating effect of my manganese-containing preparation.

The following specific examples will further illustrate my invention.

EXAMPLE 1

A 100-gram sample of #6 residual oil with an ash content of 0.075 percent by weight, a vanadium content of 225 parts per million and a sulfur content of 2.3% is ashed down in a 25-20 stainless steel flat-bottom dish.

To another 10-gram sample of the above fuel oil, there was added 0.0013 percent by weight of a manganese-containing preparation (manganese oxide complex) made by mixing in a stainless steel vessel equipped with a Lightnin' stirrer to provide agitation, 300 pounds of manganous oxide, 9.5 pounds of a 40 percent by weight solution of barium alkyl aryl sulfonate of 1010 molecular weight and containing 6.5 percent by weight of barium, 10.4 pounds of an aromatic extract oil derived from distilling off the solvent of the bottoms left during the solvent extraction of a lubricating oil fraction where the aromatic extract left in the bottoms was recovered, and finally 3.5 gallons glycerol, followed by ball milling for 48 hours the mixed manganese-containing preparation, the final product containing 25 percent by weight of manganese being fluid, stable and pumpable.

Identical samples were then prepared containing 0.004 percent by weight of a 6 percent concentrate of manganese naphthenate sufficient to supply 15 parts per million by weight of manganese in the fuel oil; another sample was prepared containing 15 parts per million of manganese by adding 0.0013 percent by weight of manganese cyclopentadienyl tricarbonyl containing 25% by weight of man-

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After the four fuel oil preparations described above were ashed down, they were placed in a muffle furnace at a temperature of 1350° F. for a period of 8 hours, then removed, cooled slowly and the characteristics of the ashes as tabulated below in Table I were determined by inspection.

To show the effects of adding higher concentrations of manganese to the same residual fuel oil above, 750 parts per million of manganese derived from the manganese oxide complex of this invention were added, and to an identical fuel oil 750 parts per million of manganese derived from manganese naphthenate were added; and to another identical fuel oil 750 parts per million of manganese derived from manganese cyclopentadienyl tricarbonyl were added; and these were similarly tested.

EXAMPLE 2

A residual fuel oil containing 0.05% by weight of vanadium, 150 parts per million vanadium and 1.0% sulfur was ashed down as in Example 1 and compared (Table I) with the same ashed down fuel oil to which was added the manganese-containing preparation of this invention, the ratio of Mn:V being 1:10 in this example.

EXAMPLE 3

A fuel oil having an ash content of 0.08%, a vanadium content of 315 parts per million and a sulfur content of 0.32% was likewise treated as in Example 2 with the manganese-containing preparation of this invention, at a Mn:V ratio of 1:7; see also Table I.

TABLE I.—FUEL-ASH TEST

Number	Fuel description	Source of manganese additive	Parts per million manganese in fuel	Characteristics of ash at 1,250° F.
1	Base fuel, Example 1		0.0	Hard, tenaciously adhering to dish, noncrushable.
2	do.	Manganese oxide-complex	15	Flaky, loose, crushable.
3	do.	Manganese naphthenate	15	Hard, adhering to dish, noncrushable.
4	do.	Manganese cyclopentadienyl tricarbonyl	15	Do.
5	do.	Manganese oxide-complex	750	Loose, finely powdered, no adherence to dish.
6	do.	Manganese naphthenate	750	Adheres partly to dish, semicrushable.
7	do.	Manganese cyclopentadienyl tricarbonyl	750	Do.
8	Base fuel, Example 2		0.0	Hard, dense, adhering.
9	do.	Manganese oxide complex	15	Loose, crushable, nonadhering.
10	Base fuel, Example 3		0.0	Hard, dense, adhering.
11	do.	Manganese oxide complex	45	Loose, crushable, nonadhering.

EXAMPLE 4

To a sample of reground coal slag passing a 20 mesh screen, these deposits having been removed from the first pass sections of the furnace where the surface temperatures averaged 1850° F., there is added a powdered manganese oxide-containing complex prepared by grinding in a porcelain ball mill for 40 hours a combination of 840 pounds of an 85 percent by weight concentrate of a manganous oxide-containing raw materia, 16 gallons of a 44 percent by weight concentrate of a barium alkyl-aryl sulfonate of 975 degree molecular weight and containing 14 percent by weight of barium, 20 pounds of a polyacrylamide polymer of 10,000 molecular weight and 10 pounds of ground mica. The finely ground, free flowing powder then is screened through a series of fine screens to give a material having an average particle size of 2 microns, within the range of 0.5 to 5 microns. A second portion of the above ground and screened slag was left untreated, and a third portion of the screened slag was likewise treated with commercially available manganous oxide. In each

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case the ratio by weight of manganese to that of the slag was 1:0.35. The mixtures of slag and additive then were placed in a muffle furnace and heated for 2 hours at 2050° F. After the dishes were allowed to cool slowly, the nature of the residue in the dishes was determined by inspection.

The above coal ash sample that was removed from the furnace tubes, and referred to as "slag" above, had the following composition:

	Percent
10 Silica	41.6
Ferric oxide	19.4
Alumina	17.3
Calcium oxide	8.7
15 Sulfur trioxide	8.2
Potassium oxide	1.7
Sodium oxide	1.0
Magnesium oxide	1.2
Titanium oxide	0.8
20 Undermined	0.1
	100.0

EXAMPLE 5

A sample of fly ash from the same boiler discussed in Example 4 above was similarly treated with the manganese oxide preparation described above, as well as with commercial manganous oxide and the test results evaluated at a temperature of 1950° F. as in Example 4 above and at the same ratios as above.

55	The fly ash had the following fusion temperatures before treatment:	° F.
	Initial deformation	1800
	Softening (H=w)	1850
60	Softening (H=½w)	1900
	Fluid	1940

EXAMPLE 6

The sample of coal, from which the above fly ash sample of Example 5 and the slag sample of Example 4 were obtained, wash ashed down and the resulting inorganic residue was mixed with the manganese oxide preparation described above in Example 4 and to a third sample of coal, a commercial manganese naphthenate was added. The test temperature in the muffle furnace was 1950° F.

The ash obtained after combusting the above coal, representing 12.5% of the coal, contained 16.5% ferric oxide and 2.8% potassium and sodium oxide.

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The coal sample that formed the origin of the tests shown in Examples 4, 5 and 6 had the following composition:

	Percent	
Moisture -----	5.0	5
Sulfur -----	2.9	
Ash -----	12.4	
Volatiles -----	34.1	
Fixed carbon -----	45.6	
	100.0	10

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EXAMPLE 11

The beneficial additive combination consisted of 70 parts by weight of a precipitated magnesium hydroxide precipitated from sea water and calcined and having an average particle size of 1 micron, 10 parts of powdered mica passing a 40 mesh screen, 7.5 parts by weight of finely powdered antimony oxide and 12.5 parts by weight of the manganous oxide preparation of Example 4. The ratio of slag to additive was 0.5 to 1.0.

The following Table II describes the results of the "slag Inhibiting Test" carried out for Examples 4 through 11.

TABLE II.—SLAG INHIBITING TEST
[Slag-forming constituent]

Number	Description	Source of manganese	Furnace temperature for testing (° F.)	Characteristics of ash (appearance)
1.....	Coal slag of Example 4.....	None.....	2,050	Hard, grainy, adherent and noncrushable.
2.....	do.....	Commercial manganous oxide.....	2,050	Do.
3.....	do.....	Manganous oxide complex.....	2,050	Soft, powdery, nonadherent, and easily crushable.
4.....	Fly ash of Example 5.....	None.....	1,950	Hard, grainy, adherent and noncrushable.
5.....	do.....	Commercial manganous oxide.....	1,950	Do.
6.....	do.....	Manganous oxide complex.....	1,950	Soft, powdery, nonadherent and easily crushable.
7.....	Coal of Example 6.....	None.....	1,950	Dense, adheres to dish, semicrushable.
8.....	do.....	Manganous naphthenate.....	1,950	Dense, adheres partially to dish, slightly crushable.
9.....	do.....	Manganous oxide complex.....	1,950	Loose, powdery, nonadherent and extremely fine.
10.....	Coal slag of Example 7.....	None.....	1,900	Dense, adheres to itself as a lump, only slightly crushable.
11.....	do.....	Manganese-oxide complex with magnesium hydroxide.....	1,900	Flaky, small platelets, non-adhering, crushable.
12.....	Coal slag of Example 8.....	Manganese-oxide complex with mica.....	1,900	Do.
13.....	Coal slag of Example 9.....	Manganese-oxide complex with magnesium oxide and mica.....	1,900	Do.
14.....	Coal slag of Example 10.....	Manganese oxide complex with dolomite.....	1,900	Do.
15.....	Coal slag of Example 11.....	Manganese oxide complex with magnesium oxide, mica and antimony oxide.....	1,900	Do.

EXAMPLE 7

To the coal ash sample obtained as a slag from the furnace screen tubes as in Example 4, there was admixed at a 1:1 ratio, a mixture consisting of 40 parts by weight of the manganese oxide complex described in Example 4 and 60 parts by weight of magnesium hydroxide of 5 to 40 microns particle size. The nature of the resultant residue of slag and additive was examined after firing in a muffle furnace at 1900° F.

EXAMPLE 8

An ash-additive test was carried out as in Example 7, but the beneficial additive in this case consisted of 75 parts by weight of ground mica passing a 40 mesh screen and 25 parts by weight of the manganous oxide complex described in Example 7.

EXAMPLE 9

A test was carried out as in Examples 4, 7 and 8, but the beneficial additive contained 65 parts by weight of magnesium oxide, 20 parts by weight of finely ground mica and 15 parts by weight of the manganous oxide complex described in Example 4 above. The ratio of slag to to additive was 0.75 to 1.0.

EXAMPLE 10

The beneficial additive combination consisted of 70 parts by weight of freshly ground dolomite to pass a 40 mesh screen and 30 parts by weight of the manganous oxide complex of Example 4. The ratio of slag to additive was 0.65 to 1.0.

EXAMPLE 12

The fuel oil of Example 2 above was subjected to an 8-hour micro gas turbine combustion test as described under Test Methods. A 25–20 stainless steel test specimen was subjected to the hot furnace exit flue at 1350° F. in order to determine the effectiveness of the manganese oxide complex to reduce high temperature corrosion and ash buildup. The SO₃ acid content of the exit gases also was monitored. The untreated fuel oil then was compared with the same three products as shown in Example 1 at a concentration of 75 parts per million manganese in the fuel oil, or a ratio of Mn:V of 0.5:1.

EXAMPLE 13

The fuel oil as shown in Example 1 was combusted in a micro gas turbine as described under test methods above. The untreated fuel oil was then compared with the same fuel oil to which was added a magnesium-containing product having 20% magnesium in the form of dispersed particles derived from magnesium oxide and magnesium hydroxide with a particle size range of 1 to 40 microns, 90% of which were greater than 10 microns. The ratio of magnesium to vanadium in the fuel was 1.5 to 1. In the third test trial, the fuel oil containing the magnesium preparation described above was likewise combusted in the furnace but every 2 hours, the manganese preparation of this invention was injected into the fuel line for a period of 5 minutes at a feed rate to supply 450 parts per million of manganese to the fuel during the 5 minute on-cycle period when the manganese was being injected. The fuel consumption rate was 0.02 gal./hr. and at an average atom weight ratio of Mn:V of only 0.25 to 1. The 25–20 stainless steel specimens were maintained at 1350° F.

The results of these tests of Examples 12 and 13 are set forth in Table III.

TABLE III.—ACCELERATED GAS TURBINE CORROSION, SLAG AND COMBUSTION TEST AT 1,350° F.

Number	Fuel description	Additive	Parts per million manga- nese in fuel	Corro- sion weight loss mg./ sq. in.	Deposits		SO ₃ (parts per million)
					Mg./ sq. in.	Characteristics	
1.....	Base fuel Example 2.....	None.....	0.0	45	55	Hard, molten scale.....	40
2.....	do.....	Manganese oxide-complex, Example 12.....	75.0	9	25	Light, powdery ash.....	15
3.....	do.....	Manganese naphthenate, Example 12.....	75.0	20	75	Molten scale, fused.....	52
4.....	do.....	Manganese cyclopentadienyl tricarbonyl, Ex- ample 12.....	75.0	15	70	Grainy, crusty.....	35
5.....	Base fuel Example 1.....		0.0	62	95	Hard, molten adhering..	90
6.....	do.....	Magnesium (as oxide and hydroxide).....	0.0	15	60	Light, powdery ash.....	65
7.....	do.....	Magnesium (as oxide and hydroxide) plus inter- mittent feed of manganese oxide complex.....	140.0	3	12	Very light, fluffy ash.....	15

¹ Average treatment rate.

EXAMPLE 14

The fuel oil of Example 1 was burned in a furnace operating at 2050 p.s.i.g. with superheater and reheat temperatures of 1000° F. The SO₃ content of the stacks was determined initially with the untreated fuel oil and then with the manganese containing invention described herein where the fuel oil contained 15 parts per million of manganese. The untreated fuel resulted in a stack concentration of 95 parts per million of SO₃ which compared to only 45 parts per million with the manganese-treated fuel.

EXAMPLE 15

A fuel oil composition as shown in Example 2 was burned in the furnace described under Example 14 above. After three months, the superheated and reheat sections of both furnaces were compared with the results that in the untreated fuel the superheater and reheat sections showed a buildup of a hard tenacious and adhering slag whereas with the manganese addition, there was no buildup and only a fine light tan powder evident on the heater.

EXAMPLE 16

A sample of synthetic slag prepared from vanadium pentoxide and sodium sulfate containing 25 percent vanadium, 15 percent sodium and 9 percent sulfur, each by weight, was treated with (1) manganese cyclopentadienyl carbonyl, (2) MnSO₄·7H₂O, (3) manganese naphthenate, (4) MnO, (5) Mn₃O₄, (6) MnO₂, (7) KMnO₄, (8) the manganese oxide complex described in Example 1. In each case the ratio of slag to Mn by weight was 1:0.25, with the results set forth in the following Table IV.

Table IV.—Slag inhibiting test with synthetic slag

Number	Slag description	Source of manganese additive	Ratio of atom weights of Mn:V	Characteristics of ash at 1,350° F.
1.....	Na-V-S slag of Example 16, treated.....	Mn cyclopentadienyl tricarbonyl.....	1:1	Dense, hard flakes.
2.....	do.....	MnSO ₄ ·7H ₂ O.....	1:1	Hard, corrosive.
3.....	do.....	Mn naphthenate.....	1:1	Dense flakes, adheres slight, semicrushable.
4.....	do.....	MnO.....	1:1	Crushable flakes, semiladherent.
5.....	do.....	Mn ₃ O ₄	1:1	Somewhat harder than 4 above.
6.....	do.....	MnO ₂	1:1	Denser and harder than 4 above.
7.....	do.....	KMnO ₄	1:1	More dense and corrosive than blank in 9 below.
8.....	do.....	Manganese-oxide complex of Ex- ample 1.....	1:1	Loose, powdery, nonadhering.
9.....	Na-V-S-slag of Example 16, untreated.....	None.....	0:1	Hard, dense, adhering and noncrushable.

EXAMPLE 17

A deposit sample taken from the first pass tubes of a furnace operating with superheat temperatures of 900° F. in a marine pressurized furnace was reground to pass a 10 mesh screen. One sample was treated with manganese naphthenate; another portion was treated with manganese acetyl acetate; another sample with a slurry of manganese oxide in kerosene and the last sample with the manganese oxide complex of Example 1. The results are that only with the manganese-containing material of this invention was there a residual fine powder that did not adhere to the metal crucible.

EXAMPLE 18

A sample of deposits taken from the first pass of a coal fired Riley Spreader Stoker furnace was mixed with

the manganese-containing powder complex described in Example 4 to give a ratio of deposits to that of Mn of 1:0.25. Another sample of these deposits was treated with magnesium oxide of 10–20 micron particle size and another sample was treated with talc of 1 to 5 micron particle size.

EXAMPLE 19

A 1 gram sample of carbon black was mixed in a porcelain dish with 0.5 gram of the manganese oxide complex of Example 1 and tested by the Soot-Ignition Test described under the Test Methods. An untreated carbon black sample is identically run for the purpose of comparison.

The results of a soot-ignition test carried out with Examples 18 and 19 are shown in the following Table V.

TABLE V.—SOOT-IGNITION TEST

Number	Deposit description	Additive	Percent com- bustibles in deposit	
			Ini- tially	After treat- ing ¹
1.....	First pass slag de- posits, Example 18, untreated.....	None.....	14	12
2.....	Same as 1, but treated.....	Manganese oxide com- plex of Example 4.....	14	1
3.....	do.....	Magnesium oxide.....	14	12
4.....	do.....	Talc.....	14	12
5.....	Carbon black, un- treated.....	None.....	95	80
6.....	Carbon black, treated.....	Manganese oxide complex of Example 4.....	95	7

¹ With additive, and firing for 150 minutes at 925° F.

EXAMPLE 20

A fuel oil of 2000 Redwood seconds viscosity with an ash content of 0.01 percent, a vanadium content of 10 parts per million and a sulfur content of 1.2 percent was treated in a porcelain dish with the manganese oxide complex described in Example 1 to supply a manganese concentration of 110 parts per million. After burning off the residual fuel, the dish containing the fuel oil residue was placed in a muffle furnace at 925° F. as described under the Test Methods, Fuel Oil Combustion Efficiency Test. An untreated fuel was run for comparing the results with the above. Another sample was prepared of the fuel oil to which was added only barium alkyl-aryl sulfonate to supply 275 parts per million barium to the fuel and a fourth sample was prepared to which a 50% manganous

oxide slurry in kerosene was added to the fuels to supply 110 parts per million of manganese. The results after ignition in the muffle furnace are shown in Table VI, "Fuel Oil Combustion Efficiency Test."

TABLE VI.—FUEL OIL COMBUSTION EFFICIENCY TEST

Num- ber	Fuel description	Source of manganese	Parts per million manga- nese in fuel	Percent burnoff at 925° C. after 2 hours
1.....	Residual fuel, Example 20.	None.....	0.0	10
2.....	do.....	Manganese oxide complex, Example 1.	110.0	90
3.....	do.....	Barium alkyl aryl sulfonate of Ex- ample 1 to supply 275 parts per million barium to fuel.	0.0	110
4.....	do.....	A 50% slurry of manganous oxide in kero- sene.	110.0	35

¹ Formed a hard crust on porcelain crucible.

EXAMPLE 21

In a marine boiler operating at superheat steam temperatures of 700 to 750° F. the consumed residual fuel with an A.P.I. gravity of 10, and containing .07 percent ash content, 220 parts per million vanadium, 2.1% sulfur was treated with the liquid manganese oxide complex of Example I at a treatment rate of 1 gallon per 600 barrels of fuel. Several alternate voyages were made wherein the fuel oil was treated, then untreated, and the cycles continued so that a comparison could be made of the appearance of the boilers, the stacks and the fuel consumption in each case.

EXAMPLE 22

A marine boiler operating at 850° F. burning a residual fuel of 0.025% ash, vanadium content of 85 parts per million and a sulfur content of 2.15% was treated with the liquid manganese oxide complex of this invention as described in Example 1 to supply 90 parts per million manganese to the fuel. The results are described in Tables VII and VIII.

TABLE VIII.—IN-PLANT MARINE TRIOL—850° F. SUPERHEAT STEAM

Num- ber	Fuel description	Parts per million manga- nese in fuel	Atom ratio of Mn:V	Appearance of deposits on superheater tubes
1.....	Residual fuel of Example 22, un- treated.	None	0:1	Hard, dense, slag. ¹
2.....	Same as 1, but treated with manganese oxide complex.	45	1:1	Only soft. ²

¹ Covering over 75% superheater banks with heavy bridging in over 50% of tubes.

² Powdery and loose deposits over superheater banks, with less than 10% bridging.

As set forth above in the preferred examples of the invention, barium is the source of the cation but other metals as the source of the cation are applicable although less effective. Examples showing metals alternative to barium as the metal of the coagent salt in the making of the composition of the present invention are as follows:

EXAMPLE 23

To a 100 gram sample of the fuel oil in Example 1, there was added 0.0013% by weight of a manganese-containing preparation made by mixing and shearing in a ball mill 300 lbs. of manganous oxide, 15 lbs. of 30% by weight solution of calcium alkyl-aryl sulfonate of 910 molecular weight and containing 2% by weight of calcium, 8.5 lbs. of a naphthenic-derived oil having a flash point of 370° F. and finally 10 gallons of a 50% aqueous solution of ethylene glycol. The mixture after ball milling for 48 hours and screened through a 100 mesh filter contained 25% by weight of manganese as a fluid, stable and pumpable material.

EXAMPLE 24

A preparation identical to that in Example 23 was prepared but with the substitution of 10 lbs. of a commercially available manganese tall oil fatty acid soap containing 6% by weight of manganese.

EXAMPLE 25

A preparation identical to that in Example 23 was made but substituting 10 lbs. of a 35% by weight solution of ammonium alkyl-aryl sulfonate of 450 molecular weight for the calcium alkyl-aryl sulfonate in the preparation.

EXAMPLE 26

A preparation similar to Example 1 above was made but substituting on a weight basis 50% of a nonmetallic emulsifier, Twitchell Base 8240, obtained from Emery Industries. In other words, 50:50 of the barium alkyl-aryl sulfonate with the emulsifier.

Each of the preparations in Examples 23 to 26 was subjected to the fuel ash test method as described in test procedures, and the results are shown in the following Table IX.

TABLE VII.—IN-PLANT MARINE TRIALS

Number	Fuel description	Source of manganese	Parts per million Mn in fuel	Appearance of—		Fuel con- sump- tion (bbls./ hr.)
				Stacks	Boilers	
1.....	Residual fuel.....	None.....		Grey plume.....	Crust deposits on tubes.....	9.3
2.....	Same as 1, but treated, 1st cycle.....	Manganese oxide complex of Example 1.....	15	Clear.....	Free of any deposits.....	8.9
3.....	Same as 1, untreated, 2nd cycle.....	None.....		Grey plume.....	Crust deposits on tubes.....	9.15
4.....	Same as 1, but treated, 2nd cycle.....	Manganese oxide complex of Example 1.....	15	Clear.....	Free of any deposits.....	8.8

TABLE IX.—FUEL-ASH TEST WITH RESIDUAL FUEL OIL

Number	Coagent for activating the manganese	Source of manganese additive	Parts per million manganese in fuel	Characteristics of ash at 1,250° F. after 24 hours
1.....	Barium alkyl-aryl sulfonate of Example 1.....		0.0	Hard, dense deposits, sticks to test crucible.
2.....	Barium alkyl-aryl sulfonate of Example 1.....	Manganese oxide complex.....	15.0	Flaky, loose, crushable deposits.
3.....	Calcium alkyl-aryl sulfonate of Example 23.....		0.0	Hard, dense, adhering deposits.
4.....	Calcium alkyl-aryl sulfonate of Example 23.....	Manganese oxide complex.....	15.0	Crushable deposits; large-sized flakes.
5.....	Manganese tall oil fatty acid soap as in Example 24.....		0.2	Hard, dense, adhering deposits.
6.....	Manganese tall oil fatty acid soap as in Example 24.....	Manganese oxide complex.....	15.0	Crushable deposits; large-sized flakes.
7.....	Ammonium alkyl-aryl sulfonate as in Example 25.....		0.0	Hard, dense, adhering deposits.
8.....	Ammonium alkyl-aryl sulfonate as in Example 25.....	Manganese oxide complex.....	15.0	Dense deposits, but can be crushed—semiadhering.
9.....	A 50-50 weight mixture of barium alkyl aryl sulfonate of Example 1 with Twitchell Base 8240.....	do.....	15.0	Large flakes of crushable and nonadherent deposits.

As shown in Table IX the complex of the manganese with the barium alkyl-aryl sulfonate, which as shown above gives the greatest heat of reaction, also results in the greatest reduction of hard ash slag deposits. The activating effect of the barium soap is thus found to be greater than that which is obtained with other alternative metal sulfonates, such as the calcium or the manganese or the ammonium sulfonates, these alternative surfactants being, however, applicable in varying degrees to accomplish the objects of the invention. Also as shown above in Table IX, substituting in part a nonmetallic emulsifier such as Twitchell Base 8240 for a portion of the barium sulfonate decreases the activating effect of the barium, but nevertheless gives a measure of improvement in accomplishing the object of the invention.

The additive composition of the invention, in addition to the uses and the combinations thereof with the liquid and solid fuels and the burner mediums described above have other important uses and applications as follows:

The additive composition may be used with refinery gases, particularly those containing any quantities of sulfur. In this case the additive would prevent the corrosion that often occurs in process heaters that are tied in with waste recovery boilers again due to the SO₃ that forms from the sulfur. Likewise even the burning of refinery gases can sometimes result in poor combustion; and again the powdered manganese or the liquid manganese preparation of this invention may be used to overcome this problem. In these cases the liquid manganese preparation would be aspirated and the powdered preparation would be air blown into the furnace.

Another use for the invention would be with supercritical and high temperature boilers burning natural gas, even where no sulfur and no vanadium or sodium are present. When the temperatures in the furnace reach 3,000° F., a serious air pollutant, NO, forms from the nitrogen present in the combustion air. The powdered additive composition containing manganese would be employed to reduce the amount of NO (and NO₂) formed and would similarly be blown into the furnace. The latter is an "in-flame" reaction, rather than occurring on the tubes or wall surfaces. For this reason, the additive composition described herein would be well suited since it is a true combustion additive.

The powdered manganese preparation of this invention could also be combined with from 1% to 50% of finely ground powders of the following:

aluminum metal, zinc metal, manganese metal, iron metal, magnesium metal, or nickel metal,

the purpose of these metals in their metallic form being to form an in-situ reaction that would keep a reducing atmosphere around the nitrogen, N₂, to prevent it from reacting with the oxygen in those critical, high temperature, large furnace boxes, with otherwise would form nitrogen oxide (NO) and which would show up as a yellow to brown plume.

Another useful innovation of the disclosed manganese-containing additive would be in pulp and paper industries in the burning of black liquors. The effluent gases are high in sodium sulfates as well as unburned carbons. Here again the disclosed manganese-containing preparation would prevent the formation of hard slags on the heat exchange tubes in the effluent sections of the furnaces, at the same time that it would prevent the unburned hydrocarbons from going out into the atmosphere. Particularly suited for this would be the combination of the silica with the manganese-containing preparation in the powdered form as described above. For this use, the liquid preparation would be added to the black liquor and the powdered preparation would be blown into the furnace.

In a further extension of the use of this manganese-containing preparation with both liquid fuels and coals, it also may be desirable to inject the additive directly into the furnace, independent of the fuel, preferably where the gas temperatures are between 600 to 1000° F. It then would react directly with the exhausting gases or coat the tubes and wall surfaces. This is important because it would be a means of protecting the economizers, the preheaters and the stacks in the furnace, as well as contributing to the reduction of acidic and combustible effluents from the stacks which are of importance for air pollution control.

The manganese additive of this invention can also be used along with other materials that are known to be effective for combining with SO₂ to reduce sulfur dioxide air pollution emitted from fuel fired burners. The manganese preparation dispersion of the present invention would be used for this purpose with dispersions of lime or limestone or dolomite injected with the furnace fuel or added to the furnace.

I claim:

1. An activated manganese-containing additive composition for fuel oils which contain a substantial amount of vanadium as well as alkali-, iron- or sulphur-containing coals, for retarding the corrosiveness and the slag buildup of the ash of such fuel oils and coals upon combustion thereof, comprising a complex prepared by reacting a manganese compound selected from the group of oxides, hydroxides, carbonates and mixtures thereof with an oil soluble coagent metal salt, the atomic weight ratio of said manganese to the metallic element in said oil soluble coagent metal salt being in the range of 100:0.1 to 100:3.0, the said complex reduced to a particle size in the range of 0.25 to 20 microns, the said coagent metal salt being a metal salt of an alkyl-aryl sulphonic acid in which the metallic element is selected from the group consisting of barium, calcium, cadmium, magnesium, iron, zinc, sodium, potassium, lead, nickel, tin, aluminum, strontium, chromium, zirconium, manganese, cobalt, and copper.

2. The activated manganese-containing composition of claim 1, added in a small amount to a major amount of a residual petroleum fuel containing vanadium which yields a corrosive and ash-depositing vanadium-containing slag upon combustion.

3. The composition of claim 2 wherein the fuel is a solid residual petroleum fuel.

4. The composition of claim 3, in which the atom ratios of manganese in the composition to vanadium in the fuel is of the order as low as 0.25:1 and 0.5:1.

5. The activated manganese-containing composition of claim 1, added in a small amount to a major amount of fuel selected from the group consisting of alkali-containing coals, iron containing coals, and sulfur containing coals for rendering noncorrosive and nonslagging such coals which contain an amount of alkali metal, iron and sulfur as normally to yield a corrosive or slag forming ash upon combustion.

6. The composition of claim 5, wherein the additive composition comprises a major proportion of the manganese compound of the particle size of 0.25 to 20 microns comixed with a minor amount of the coagent metal salt, and the final manganese-coagent complex is in the form of a powder.

7. The activated manganese-containing additive composition of claim 1, in which the manganese compound is finely ground and then reacted with the oil soluble coagent metal salt in a carrier solvent.

8. The activated manganese-containing composition of claim 1, in combination with a magnesium-containing compound selected from the class consisting of magnesium oxide, magnesium hydroxide and magnesium carbonate, where the magnesium compound is fed into a burner medium such as a furnace, turbine or other fuel combustion chamber and the manganese compound is added to the same boiler medium.

9. The activated manganese-containing composition of claim 1, in combination with a material to be concurrently burned therewith selected from the group consisting of silica, dolomite, kaolin, alumina, montmorillonite and pyrophyllite.

10. The activated manganese-containing composition of claim 1, added in a small amount to a major amount of sulfur containing coals, and fuels that yield toxic or corrosive oxides of sulfur upon combustion.

11. The activated manganese-containing composition of claim 1, in combination with a light hydrocarbon distillate fuel, added directly or concurrently with the fuel to a burner medium for the fuel such as the furnace or furnace box.

12. The activated manganese-containing composition of claim 1, added in a small amount to a fuel oil containing burner medium in which fuel burned at high temperatures develop gases of the class consisting of SO_3 , SO_2 , NO and NO_2 .

13. An activated manganese-containing additive composition for fuel oils which contain a substantial amount of vanadium as well as alkali-, iron- or sulphur-containing coals, for retarding the corrosiveness and the slag build-

up of the ash of such fuel oils and coals upon combustion thereof, comprising a complex of a manganese compound selected from the group of oxides, hydroxides, carbonates and mixtures thereof reacted with an oil soluble coagent metal salt, the atomic weight ratio of said manganese to the metallic element in said oil soluble coagent metal salt being in the range of 100:0.1 to 100:3.0, the said complex reduced to a particle size in the range of 0.25 to 20 microns, the said coagent metal salt being a metal salt in which the metallic element is barium, and an organic acidic compound that forms an oil soluble salt with barium selected from the class consisting of (1) the fatty acids of at least 5 carbon atoms, (2) alkyl aryl sulfonic acids, (3) long chain alkyl sulfuric acids and (4) petroleum naphthenic acids.

14. An activated manganese-containing additive composition for fuel oils which contain a substantial amount of vanadium as well as alkali-, iron- or sulphur-containing coals, for retarding the corrosiveness and the slag buildup of the ash of such fuel oils and coals upon combustion thereof, comprising a complex of a manganese compound selected from the group of oxides, hydroxides, carbonates and mixtures thereof reacted with an oil soluble coagent metal salt, the atomic weight ratio of said manganese to the metallic element in said oil soluble coagent metal salt being in the range of 100:0.1 to 100:3.0, the said complex reduced to a particle size in the range of 0.25 to 20 microns, in which the metal of the said coagent metal salt is selected from the class consisting of calcium, magnesium, sodium, potassium, strontium, beryllium, zinc and barium and the organic acid that forms an oil soluble salt with the metal is selected from the class consisting of sulfonic acids of petroleum origin and carboxylic acids selected from the class consisting of tall oil fatty acid, naphthenic acids, octoic acid and 2-ethylhexoic acid.

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Disclaimer and Dedication

3,692,503.—*Ira Kukin*, West Orange, N.J. ACTIVATED MANGANESE CONTAINING ADDITIVE FOR FUELS. Patent dated Sept. 19, 1972. Disclaimer and Dedication filed Mar. 10, 1983, by the assignee, *Economics Laboratory, Inc.*

Hereby disclaims and dedicates to the Public the entire term of said patent.
[*Official Gazette March 12, 1985.*]