United States Patent Office

2,793,945

Patented May 28, 1957



2,793,945

# RESIDUAL FUELS

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No Drawing. Application January 11, 1954, Serial No. 403,435

9 Claims. (Cl. 44—76)

This invention pertains to a method for reducing the corrosiveness of vanadium-containing ash that is produced by the combustion of residual type hydrocarbon fuels. It further pertains to ash compositions of reduced corrosiveness and to residual-type fuel compositions which form substantially non-corrosive ash when they are burned. It especially relates to the phosphorizing of residual petroleum fuels that contain vanadium whereby the ash derived from these fuels is substantially non-corrosive towards iron, steel, steel alloys, and other ferrous metals. It also especially relates to the inclusion of phosphorus within the ash that is derived from the combustion of residual petroleum fuels whereby the ash becomes substantially non-corrosive.

This is a continuation-in-part of our co-pending application Serial Number 259,484, filed December 1, 1951, now abandoned.

The term "phosphorizing" as used in this specification is intended to mean the incorporation of phosphorus in a soluble form within a fuel oil fraction or a vanadium-containing residual fuel oil. Thus, the phosphorus composition may be added to the fuel or it may be formed in situ. In any case a fuel is "phosphorized" by the addition thereto or the formation therein of a phosphorus composition which is soluble in the fuel.

Residual fuels derived from petroleum find wide use in marine and stationary steam power plants where the high B. t. u. content and low cost of such fuels make them very attractive economically. These fuels may be in the residual products or blends thereof that are obtained from refining operations such as the distillation of crudes, the flashing or distillation of cracked products and redistillation operations. They may consist of either virgin or cracked hydrocarbons. Inasmuch as the viscosity of a residual fuel is one of its more important properties, it is sometimes necessary, where a particular residuum is too viscous, to dilute it with a low viscosity distillate fraction. It is apparent then that residual fuels may contain distillate fractions as well as residues but in general they consist primarily of residual material.

Residual fuel oils are also known in the trade as bunker fuel oils. They are characterized roughly as boiling above 400° F. The United States Department of Commerce recognizes two grades of residual fuel (No. 5 and No. 6) in its classification system for petroleum fuels. The No. 5 grade is essentially a distillate fuel with small amounts of residual materials. It contains relatively little ash-forming material.

The No. 6 fuel is usually a true residual fuel containing a substantial amount of ash up to .10% by weight or more. It is this grade with which this invention is primarily concerned. The No. 6 or bunker fuel grade has a gravity range of about 9 to 15° A. P. I., a viscosity range of about 30 to 300 at 122° F. (Saybolt Furol), a minimum flash point of 150° F. and a Conradson carbon residue of at least 0.5%.

This invention is concerned primarily with the ash content of residual or bunker fuel oils. The amount and type of ash formed by a residual fuel oil during combustion vary primarily with the ash content and the origin of the crude oil from which it was derived. Crude oils when burned may form up to about 3% by weight of ash and the ash-forming constituents are concentrated almost entirely in the residua by refining operations performed on the crudes. Residual fuels, as such, however, generally contain less than 0.1% by weight of ash.



Chemical analyses of fuel oil ash reveal that a wide variety of chemical constituents may be found. Among these are silicon, aluminum, lead, copper, iron, calcium, magnesium, nickel, vanadium, molybdenum, and tungsten. Of primary interest here is the vanadium content which may be up to 80%, calculated as $V_2O_5$, by weight of an ash.

The vanadium (e. g. $V_2O_5$) content of ash derived from domestic crude oils will vary in general from about 0. to 20%. Residual fuel oils obtained from Middle East crudes produce ash with vanadium contents of 14 to 45%, while in the case of South American crudes, the value will usually be in the range of 20 to 80%. At the present time it is not known exactly what chemical forms or compounds of vanadium actually exist in these oils.

The amount of ash in a residual fuel oil, and, in particular, its vanadium content (generally expressed, conventionally in the results of chemical analysis, as vanadium pentoxide content) have recently become a matter of great importance. This is particularly true in the power generation field where the vanadium contained in the fuels employed has been found to cause extensive corrosion in power equipment that operates at high temperatures. Examples of such high temperature equipment include the gas turbine, the mercury boiler and extremely high temperature and pressure steam boilers. All of these installations have metal parts which are exposed at temperatures above 1000° F. directly to the gases produced by the combustion of residual fuel. In the case of the boilers, the metallic parts include such items as the boiler tubes and super heater tubes. In the case of the gas turbine, the burner chamber, turbine nozzles, and blading are among the parts subjected to these conditions. In general, extensive corrosion of all of these parts has occurred, particularly when a residual fuel forming an ash of high vanadium content was employed.

In an effort to combat the corrosion described above, stainless steels and other heat resistant alloys have been used in the construction of the parts affected, but little success has yet been achieved along these lines. With this in mind, efforts are now being directed toward improving the quality of the fuels. All of the studies made in this direction have shown conclusively that the corrosion is directly due to the products of the vanadium compounds which become a component of the ash formed when the fuel is burned.

When a residual fuel containing vanadium compounds is burned, the vanadium apparently reacts with oxygen to form compounds such as vanadium oxides (e. g. $V_2O_5$) and vanadates. These materials are carried along with the flue gas and are in contact with and partly deposit on the metal parts of the gas turbines and boilers described earlier. Inasmuch as vanadium pentoxide has a melting point of 1274° F., this material very often is present in its liquid form and has a substantial vapor pressure at the temperatures existing in gas turbine or boiler installations. Experimental work shows that vanadium pentoxide is extremely corrosive toward even the most corrosion-resistant alloy steels at temperatures of 1200° F. and up. It has further been shown that this chemical compound is most corrosive when it is present as a fluid. It appears that vanadium pentoxide or other vanadic acid not only destroys the oxidation-resistant surface layer which normally exists on alloy steels; but it also seems to act as an oxidation catalyst, thereby

markedly increasing the rate of corrosion once it has started.

Inasmuch as one of the chief reasons for the use of residual heating oils rather than other fuel types is their low cost, it is essentially that any method for reducing the corrosiveness of the ash produced by combustion of these oils must be as inexpensive as possible. Such measures as centrifuging, filtering, distillation, and electrical or chemical desalting processes are largely out of the question for economic reasons. Lime has been added to residual fuel oils and some success in combating corrosiveness has thereby been achieved. The lime apparently reacts with the vanadium pentoxide to form a calcium vanadate which is non-corrosive toward the metal parts ordinarily subject to corrosion. Lime has the disadvantage, however, that it is insoluble in a residual fuel oil, a condition which it is desired to avoid.

In its broadest embodiment, the present invention comprises the incorporation of a phosphorus-containing composition within a vanadium-containing fuel ash in an amount sufficient to reduce the corrosiveness of the ash toward metals at temperatures in excess of about 1000° F. Of particular concern are ashes that contain more than about 1% by weight of $V_2O_5$ and that are produced by the combustion of vanadium-containing residual petroleum fuel oils. It will be noted that the vanadium in an ash, fuel or the like need not be present as $V_2O_5$, but it is generally considered to so exist for the convenient expression of analytical results. In the present description the vanadium content of an ash, fuel or other material will be expressed either as its vanadium pentoxide content or its vanadium content, although the vanadium in no case need actually be present in either of these two forms. Similarly, the phosphorus content of any given material will be expressed merely as its phosphorus content, although the phosphorus may be present in a combined form.

Substantially any phosphorus-containing composition may be added to a vanadium-containing ash of the type hereinbefore described in order to realize the benefits of the present invention; since the sole feature of the invention that must be observed lies in establishing a satisfactory ratio of phosphorus to vanadium within the ash. Thus, the amount of a phosphorus-containing composition that is added to any given vanadium-containing fuel ash must be sufficient to provide at least 1 mol of phosphorus per mol of $V_2O_5$ within the ash (e. g. 1 mol of phosphorus for every 2 mols of vanadium). While there is no theoretical upper limit as to the amount of phosphorus that may be added to an ash, it is practically desirable to limit the amount to obtain mol ratios of $P/V_2O_5$ that are less than about 10/1. (e. g. mol ratios of P/V that are less than about 5/1.) Preferred $P/V_2O_5$ mol ratios are in the range between 3/1 and 5/1.

Phosphorus may be added to a vanadium-containing ash in elemental or combined form and as a vapor, liquid or solid in order to realize the benefits of the present invention. Furthermore, the phosphorus composition may be organic or inorganic, chemically speaking. The reason for this latitude in the choice of a phosphorus composition lies in the fact that a proper $P/V_2O_5$ ratio in an ash appears to be the only feature that must be critically observed to reduce the corrosiveness of the ash toward metals at temperatures in excess of about 1000° F.

Suitable inorganic phosphorus compounds that may be incorporated within a vanadium-containing ash include the oxides, acids, and acid anhydrides of phosphorus such as $P_2O_5$, $P_2O_3$, $H_3PO_4$, $H_3PO_3$, $P_2S_3$, $P_2S_5$, etc. Preferred inorganic compounds include the oxides and oxy-acids of phosphorus. A particularly preferred compound is $P_2O_5$.

Suitable organic compounds include the alkyl, aryl and alkenyl phosphines, phosphates, phosphites, phosphonium salts, phosphine oxides, phosphonites, phosphinites, phosphonates and phosphinates. The substituted groups in each class of compounds may be identical as to their chemical type and size, or they may vary in both these respects.



Specific examples of suitable organic compounds include triphenylphosphine, triethylphosphate, triphenyl phosphate, tricresyl phosphate, diethyl octene phosphonate, triphenyl phosphine oxide, etc.

Preferred organic phosphorus compositions for inclusion in a vanadium-containing ash include the compositions that are formed by chemically combining phosphorus or a phosphorus-containing compound with petroleum, petroleum derivatives and oxygenated organic compounds. Compositions of this type may be formed by reacting a phosphorus compound such as $P_2O_5$, $H_3PO_4$, $P_2S_5$, $P_2S_3$ etc., with organic compositions such as crude oils, bright stocks, kerosenes, lube oils, gas oils, cracked paraffin waxes, alcohols, ketones, phenols, esters, phenol sulfides and the like. Conditions for carrying out such reactions and specific examples of the same will be presented in detail later in this description.

A phosphorus composition of the types described above may be added to a residual fuel oil ash in a number of different ways. Thus, it may be merely physically admixed with an ash by any conventional mixing technique. Or, it may be injected directly into the firebox or combustion chamber where the ash is formed by the combustion of the fuel oil. Again, the phosphorus composition may be sprayed or otherwise deposited on the metal surfaces which it is intended to protect from the vanadium in the fuel ash. In any case, it is mandatory that the ratio of P to V be maintained within the range of values stipulated earlier in this description.

The best mode contemplated for incorporating phosphorus within the ash which is derived from a vanadium-containing residual petroleum fuel oil consists in phosphorizing the fuel oil itself before it is burned. As defined earlier, the term "phosphorizing" as used herein is intended to mean the incorporation of phosphorus in a soluble form within a residual fuel. Thus, a fuel may be phosphorized by chemical formation therein or by the addition thereto of a soluble phosphorus-containing composition. It is particularly preferred that a soluble phosphorus composition be formed directly within a residual fuel.

It is desired that a vanadium-containing residual fuel be phosphorized to an extent such that the ratio of the number of mols of phosphorus in the ash produced by the fuel to the number of mols of vanadium calculated as vanadium pentoxide (e. g. mols $P/mols\ V_2O_5$) be in the range of 1:1 up to 10:1. The invention is particularly attractive for preventing corrosion when the ratio of the mols of phosphorus to the mols of vanadium pentoxide is between 3:1 and 5:1. It will be noted that the mols of phosphorus per mol of vanadium in an ash are desired to be kept within the range of 0.5:1 to 5:1 and preferably between 1.5:1 and 2.5:1.

When a fuel containing natural vanadium compounds and added phosphorus or phosphorus compounds is burned and an ash thereby formed, a reaction occurs to form a stable complex of undetermined composition. This complex appears to have a high melting point; in any event, it is non-corrosive towards steel and other metals at temperatures of 1200° F. and above. There is some evidence that this compound in its pure state may have a deep green or bluish-green color. It is of further interest that this complex causes the vanadium to lose its activity as an oxidation promoter.

For the purposes of this invention, the percentage by weight of vanadium (expressed as vanadium pentoxide) in a fuel may be in the range of 0.001 to 3.0%. Fuels containing .001 to .15% by weight of vanadium pentoxide are particularly contemplated. As pointed out earlier, it will be noted that vanadium is not necessarily present as vanadium pentoxide in a residual fuel or in the fuel ash, but it is more convenient to consider that such is the case for the sake of expressing analytical findings.

The residual fuel compositions described above may be realized in several ways. It should be noted first, that the vanadium is present in the fuel as a result of either natural association or contamination. In any event, it is not part of the present invention to add further vanadium to a fuel. The methods now to be described for the incorporation of phosphorus in a fuel are not intended to be exclusive but instead merely representative of the techniques that may be employed.

One method for arriving at a desired residual fuel oil composition consists in blending a soluble organic composition containing phosphorus with a residual fuel containing vanadium. These soluble organic compositions (addition agents) may be produced by reacting phosphorus or a phosphorus compound with an organic composition to form a product which will dissolve in a residual oil. Examples of phosphorus compounds which react with organic compositions to form suitable addition agents for residual fuels include the following:

Phosphorus pentoxide
Phosphoric acids
Phosphorus pentasulfide
Phosphorus sesquisulfide
Phosphorus trichloride
Phosphorus pentachloride
Phosphorus oxychloride
Phosphorus thiochloride
Phosphorus

Of the foregoing, phosphorus pentoxide and the phosphoric acids are particularly useful for the purpose. Ortho phosphoric acid ($H_3PO_4$) is especially preferred. It is available commercially in 85% concentration.

Examples of suitable organic compositions with which phosphorus or the phosphorus compounds listed above will react to form addition agents of the type described as being suitable for the purpose of this invention are as follows:

1. Petroleum and petroleum derivatives such as crude mineral oils of paraffinic, napthenic or asphaltic character and from various sources including the domestic Middle East, and South American fields and products refined from them, e. g.

Bright stock
Neutral or pale oils
Steam refined oils
Fuel oils
Kerosene
Gas oils
Cracked paraffin wax
Cracked fuel oils
Cracked gas oils
Petrolatum
Solvent extracted fractions, e. g.
  Phenol extract
  Furfural extract
Polyisobutylene
Polypropylene

2. Oxygenated organic compounds, such as

Alcohols, like octyl alcohol
Ketones
Phenols and phenates
Unsaturated esters, like ricinoleates
Partial esters of polyhydric alcohols
Phenol sulfides

Reactions between the phosphorus compounds and the organic compositions listed above may be carried out at temperatures in the range of about 100° F. to 500° F. and with reaction times of about ½ hour to 8 hours. Any unreacted phosphorus compound or insoluble matter may be filtered or otherwise separated from the desired product. It will be noted that these products may be added to an ash itself, as described hereinbefore; or they may be dissolved in a residual fuel.



A specific example of a preferred phosphorus composition of the type described above may be formed by reacting $P_2S_5$ with a bright stock. Thus, a crude Panhandle residuum which has been deasphalted and acid-treated to form a bright stock having a viscosity of about 170 S. S. U. @ 210° F. may be reacted with about 16 wt. percent of $P_2S_5$ at about 420° F. until the product has a viscosity of about 600 S. S. U. @ 210° F. This reaction generally takes about 6 to 8 hours, and the product formed possesses about 4 wt. percent phosphorus. The product may be filtered to remove any insoluble matter that may be formed in the reaction.

The soluble phosphorus-containing compounds described above may be added to a residual fuel oil directly, or they may be added to one or more of the component fractions or refinery stocks that go to make up the fuel. In any event the final fuel blend must contain an amount of phosphorus sufficient to provide between 1 and 5 mols of phosphorus per mol of vanadium in the fuel ash. It has been found that this objective may be successfully realized by utlizing this same range of mol ratios within the fuels. In other words, it has been found that by providing a residual fuel oil with sufficient phosphorus to establish a mol ratio of between 1/1 and 5/1 phosphorus to vanadium in the fuel, the ash which is formed by combustion of the fuel contains phosphorus and vanadium in the same range of molal ratios. It has further been found that the ash formed by the combustion of these fuels is markedly less corrosive toward metals at temperatures above 1000° F. It is particularly preferred that a residual fuel have a phosphorus to vanadium mol ratio between about 2.5/1 to 4/1.

A second and preferred method in which the desired fuel oil compositions may be obtained consists in reacting elemental phosphorus or a phosphorus compound directly with a residual fuel oil or with one of the component fractions of the fuel. In other words, the desired soluble, phosphorus-containing organic compositions are formed in situ in the residual oil. Inorganic phosphorus compounds which may be used for this purpose are any of those described above in connection with the preparation of soluble phosphorus compositions that may be added to a fuel.

Acids or acid anhydrides of phosphorus are especially desirable forms of phosphorus that may be reacted directly with a residual fuel oil or with one of its component fractions. The particular anhydrides which have been found to be most effective are phosphorus pentoxide and phosphorus pentasulfide, these being the anhydrides of phosphoric and thio phosphoric acids respectively. Phosphoric acid and the various thio phosphoric acids and their anhydrides are also effective. Orthophosphoric acid ($H_3PO_4$) is particularly preferred for this purpose.

In phosphorizing a residual fuel by the formation therein of a soluble organic phosphorus-containing composition, the fuel is phosphorized to the extent where the ratio of the mols of phosphorus to the mols of vanadium pentoxide in the fuel ash is between 2:1 and 10:1 and preferably 3:1 and 5:1. Many of the details and possible means for carrying out such phosphorization have been described earlier. When phosphorus or a phosphorus compound is reacted directly with a fuel, it is generally necessary that the mixture be heated until a reaction between the phosphorus or phosphorus compound and the fuel takes place. In general, it has been found that a temperature of 100 to 400° F. is necessary. A temperature in the range of 150 to 250° F. is especially preferred. Reaction times of about ½ to 8 hours are generally necessary. The reaction products may be filtered or settled if necessary to remove any insoluble matter.

Where desirable, the phosphorus or phosphorus compound may be reacted with one component of a residual fuel oil. For example, where a distillate oil is blended

with a residual oil to form a residual fuel oil it may be preferable to phosphorize the distillate fraction rather than the residual material. Likewise, when residual fractions from more than one refining operation are blended to form a residual fuel oil, it may be preferable to phosphorize merely one of these fractions. It is necessary, however, that the ratio of phosphorus to vanadium pentoxide in the final residual fuel oil blend be such that the mol ratio of phosphorus to vanadium pentoxide in the fuel ash be in the range of ratios given earlier. The amount of phosphorus that must be incorporated within the fuel itself may be readily ascertained as described earlier.

The best mode contemplated for phosphorizing a residual fuel oil in order to incorporate phosphorus within the ash which is formed by combustion of the fuel consists in reacting the fuel with $H_3PO_4$ at a temperature of about 150° F. and for a period of about 1 hour. 85% $H_3PO_4$ is very effective for this purpose.

The phosphorizing of a residual fuel oil may be carried out in any conventional refining equipment suitable for this purpose. Such apparatus as heated storage tanks, treating tanks, mixing tanks, orifice mixers and the like may be employed. Where the phosphorus compound which is reacted with or incorporated in a residual fuel oil evolves hydrogen sulfide or other odoriferous products, it may be desirable to air blow the fuel oil before marketing it.

Evidence of the beneficial effect of incorporating phosphorus within vanadium-containing residual fuel oil ash has been obtained by means of a "static oil ash corrosion test." This test, which has been found to correlate very well with full scale operation in boilers and gas turbines, is carried out in the following manner:

Place 3 grams of fuel oil ash in a No. 1 Coors Crucible, add a given quantity of additive, thoroughly mix, place a weighed steel test specimen (25 chromium/20 nickel alloy—AISI type 310 steel) in the crucible so as to be partially immersed in the ash and additive mixture, place the crucible set-up in a muffle furnace for 48 hours at 1500° F. and displace the furnace atmosphere with air on a volume basis of approximately 100:1/hour throughout the test period. At the end of the test period, remove the crucible set-up from the furnace, descale the steel test specimen electrolytically in molten caustic, wash, dry and weigh. Calculate the relative weight loss on the basis of percent weight loss for a test specimen subjected to the fuel oil ash only under the same test conditions.

Where the additive employed is contained in an oil base, the fuel oil ash and additive mixture is reduced to ash in a separate crucible, first, by coking at a low temperature (below 1000° F.) and finally by placing in a muffle furnace for one hour at 950° F. The resulting ash is removed from the furnace, pulverized and added to the crucible containing the steel specimen.

The corrosiveness of the ash produced by the combustion of a residual fuel oil containing vanadium is amply demonstrated by the data presented below in Table I. As indicated, these data were obtained using the static oil ash corrosion test described above:

TABLE I

*Effect of vanadium content on corrosiveness of fuel oil ash—static oil ash corrosion test at 1500° F.*

| Sample Tested | Pure $V_2O_5$ | Venezuelan Fuel Oil Ash | Venezuelan Fuel Oil Ash | Domestic Fuel Oil Ash | Reference (No Ash) |
|---|---|---|---|---|---|
| Composition: $V_2O_5$, wt. percent | 100.0 | 73.11 | 44.29 | 1.00 | 0 |
| Corrosiveness: Steel Specimen, percent wt. loss | 85.0 | 20.0 | 18.0 | .07 | 0.30 |



To establish the ability of the static oil ash corrosion test to predict the corrosiveness of residual fuel oil ash, residual fuels of different vanadium contents were burned in an actual burner installation. The corrosiveness of the ash produced by each fuel was determined by measuring the loss in weight experienced by steel test specimens (25 chromium/20 nickel alloy) exposed to the flue gases at a temperature of 1600° F. One such fuel containing 0.057% $V_2O_5$ caused a specimen weight loss of about 8% in 80 hours, while another fuel containing only .002% $V_2O_5$ caused less than .30% loss in the same length of time. These results substantiate the results obtained by the static oil ash corrosion test.

The beneficial effect obtained by incorporating phosphorus within fuel oil ash containing vanadium is brought out in Table II below:

TABLE II

*Effect of phosphorus concentration on corrosiveness of a fuel oil ash containing 73% $V_2O_5$*

[Static oil corrosion test at 1500° F.]

| Mol Ratio $P/V_2O_5$ | 1:1 | 3:1 | 5:1 | 7:1 | 9:1 |
|---|---|---|---|---|---|
| | Stainless Steel Specimen Relative Wt. Loss, Percent | | | | |
| No Additive | 100 | 100 | 100 | 100 | 100. |
| $+P_2O_5$ | 73 | 1.6 | 1.3 | 1.2 | no test. |
| $+P_2S_5$ | 157 | 67 | 3.0 | no test | Do. |
| $+P_2S_5$ treated Bright Stock | 245 | 26 | 2.4 | do | Do. |
| $+P_4S_3$ | | | | | 16.5. |

It will be clearly seen in Table II that the addition of phosphorus compounds to residual fuel ash containing vanadium compounds results in remarkable decreases in the corrosiveness of the ash. It may also be seen that where the mol ratio in the ash of phosphorus to vanadium pentoxide is at least 3:1, the beneficial effect of the phosphorus is especially marked. In general, little improvement is obtained until the mol ratio is at least 3:1. Indeed, corrosion is actually increased at ratios of about 1:1 in some instances.

Summarizing momentarily, the present invention teaches that the incorporation of phosphorus in a residual fuel oil ash containing vanadium results in an ash which is non-corrosive toward metals at temperatures of 1000° F. and above. This invention further describes a process whereby the corrosiveness of the ash produced by the combustion of a vanadium-containing residual fuel oil may be markedly reduced by phosphorizing the residual fuel. This phosphorization may be carried out by formation directly in or by addition to a residual fuel oil of a soluble, organic, phosphorus-containing composition.

It will be noted that it may be desirable in some instances to phosphorize a residual fuel right at the point of combustion. For example, in the case where steam or air atomizers are used to inject fuel into the fire-box of a boiler, it may be desirable to phosphorize the fuel at this point.

The following specific examples will serve to better illustrate the nature and scope of the present invention.

EXAMPLE I

Separate samples of a bunker fuel hereinafter identified as Fuel No. 359 were reacted with phosphoric acid (85%) and with $P_2O_5$ at 150–160° F. with stirring. This fuel contained 0.057 wt. percent $V_2O_5$, assuming that all of the vanadium was present as the pentoxide. Following the reaction period, the fuel samples were analyzed for their phosphorus contents. The results were as follows:

TABLE III

*Reaction studies*

[Bunker fuel (No. 359) + phosphorus compounds 1 hour at 150–160° F. with stirring]

| | +0.18% $H_3PO_4$ (85%) | +0.11% $P_2O_5$ |
|---|---|---|
| Percent P (Determined) | 0.062 | 0.054 |
| Percent P Added | 0.049 | 0.049 |

The slight discrepancy in the phosphorus analyses was very likely occasioned by experimental error.

EXAMPLE II

A residual fuel hereinafter identified as Fuel No. 1230 and containing vanadium in an amount equal to about 0.082% $V_2O_5$ was phosphorized with 0.32 wt. percent of 85% $H_3PO_4$. The reaction was carried out at 190°–200° F. with mixing over a period of about 6 hours. The phosphorus composition formed was apparently completely soluble, since no precipitation was observed.

EXAMPLE III

A number of vanadium-containing residual fuels were burned in a small scale combustion apparatus to more completely determine the corrosive effect that the ash from these fuels has upon metals. Two of the fuels were then phosphorized by reaction with $H_3PO_4$ and again burned in the combustion rig. A direct indication of the effect that phosphorus has upon the corrosiveness of vanadium-containing fuel ash was therefore made possible.

Inspections of the various fuels and ash formed by them are summarized in the following table. It will be noted that each of the fuels is identified by a separate number for the sake of simplicity.

TABLE IV

*Residual fuel inspections*

| Fuel No. | 359 | 641 | 710 [1] | 1230 | 1288 [2] | 14 | 9843 |
|---|---|---|---|---|---|---|---|
| Gravity, °API | 13.5 | 14.6 | 13.1 | 13.7 | 13.3 | 10.9 | 13.8 |
| Flash (PM), ° F | 230 | 175 | 170+ | 208 | 224 | 196 | 295 |
| Viscosity, Furol, At 122° F | 168 | 168 | 246 | 186 | 302 | 109 | 291 |
| Ash, Total, Percent | 0.09 | 0.07 | 0.16 | 0.08 | 0.20 | 0.09 | 0.07 |
| Ash, $H_2O$ Soluble, Percent | 0.06 | ------ | 0.04 | 0.05 | 0.08 | 0.06 | ------ |
| $V_2O_5$ (Calculated), Percent | 0.057 | 0.002 | ------ | 0.063 | 0.082 | 0.0009 | 0.034 |
| Sulfur, Percent | 2.39 | 1.75 | 2.45 | 2.51 | 2.95 | 0.87 | 2.35 |
| Water, By Distillation, Percent | 0.40 | Nil | 0.2 | Trace | Trace | 0.10 | 0.9 |
| Sediment, By Hot Filtration, Percent | 0.05 | 0.10 | 0.13 | 0.10 | 0.20 | 0.09 | 0.02 |
| Insol. 86° Naphtha (Mod.), Percent | 9.52 | ------ | 11.3 | 10.1 | 12.5 | 4.3 | 9.3 |
| Ash Composition—Wt. Percent Quantitative Spectro Chemical: | ** | ** | | | | | |
| Aluminum (as $Al_2O_3$) | 5.17 | 4.84 | 0.34 | ------ | 0.26 | 0.22 | 0.59 |
| Calcium (as CaO) | ------ | ------ | 1.1 | ------ | ------ | 21.14 | 2.46 |
| Copper (as CuO) | ------ | ------ | 0.21 | ------ | 0.12 | ------ | ------ |
| Iron (as $Fe_2O_3$) | 1.72 | 2.61 | 0.67 | 1.2 | 0.83 | 11.63 | 2.24 |
| Magnesium (as MgO) | 0.44 | <0.4 | 0.63 | 0.42 | 0.53 | 0.67 | ------ |
| Nickel (as NiO) | 4.38 | 0.86 | 3.2 | 6.3 | 4.2 | 0.75 | 1.05 |
| Sodium (as $Na_2O$) | 8.18 | 20.50 | 9.6 | 14 | 6.5 | 1.64 | 10.38 |
| Silicon (as $SiO_2$) | 3.18 | 0.66 | ------ | ------ | ------ | 2.80 | 0.63 |
| Sulfur (as $SO_3$) | 14.42 | 53.66 | ------ | 6.8 | 0.23 | 36.79 | 29.13 |
| Vanadium (as $V_2O_5$) | 63.7 | 2.50 | 29 | 70 | 43 | 1.00 | 44.29 |

[1] Fuel No. 359+0.18 wt. percent $H_3PO_4$ (85%).
[2] Fuel No. 1230+0.32 wt. percent $H_3PO_4$ (85%).
** By wet analysis.

In the combustion apparatus that was employed for evaluating the fuels listed in Table IV, each fuel was first preheated to a temperature of about 180° to 205° F. in a steam-heated exchanger and then passed through a 60 mesh strainer before it entered the burner. The burner was a small capacity, low pressure, air atomization burner capable of handling from 1–2 gals. per hour of residual fuel.

The combustion chamber was equipped with a brick checkerwork at its base with damper to permit control of excess air. The fuel was burned with excess air to give an approximate 23:1 air/fuel ratio. The hot flue gases passed from the combustion chamber to an insulated flue pipe in which metal test specimens (AISI type 310, 25–20 Cr–Ni, steel) were mounted on refractory holders. By inserting specimens at intervals along the flue pipe, various test temperatures could be investigated. The maximum test temperature (nearest the combustion chamber) was controlled by adjusting the burner firing rate. The flue pipe gas velocity was about 1–2 ft./sec.



Enough specimens were inserted to permit their removal at various time periods whereby their corrosion could be evaluated as a function of time and temperature. Following removal from test, the specimens were descaled electrolytically, weighed and the weight loss calculated from the original weight. The original specimens weighed from 6–9 gms. each.

The following data were obtained on test specimens that were maintained at 1600° F. for the fuels in Table IV. Since two of the fuels were burned in the apparatus both before and after phosphorization, a direct indication of the effect of phosphorizing a fuel is made possible.

TABLE V

*High temperature corrosion data*

[Percent wt. loss AISI–310 steel test specimens]

| Exposure, Hours | Fuel No. 641 | 14 | 9843 | 359 | 710 [1] | 1230 | 1288 [2] |
|---|---|---|---|---|---|---|---|
| 10 | 0.06(6*) | 0.11 | 0.26 | 1.00 | ------ | 2.29 | 0.46 |
| 20 | 0.13(21*) | 0.13 | 0.36 | 2.00 | 0.57(23*) | 4.49 | 0.61 |
| 30 | ------ | 0.16 | 0.65 | 3.05 | 0.73(32*) | 7.28 | 0.80 |
| 40 | ------ | 0.20 | 0.82 | 4.10 | ------ | 7.95 | 1.91 |
| 48 | 0.18(50*) | 0.23 | 1.33 | 4.90 | 1.46 | 10.6 | 1.89 |

[1] Fuel 359 phosphorized with 0.18 Wt.% $H_3OP_4$ (85%).
[2] Fuel 1230 phosphorized with 0.32 Wt.% $H_3PO_4$ (85%).
*Hours.

The data in Table V clearly show three things (1) that the corrosiveness of the ash from a vanadium-containing residual fuel is substantially a direct function of the vanadium content of the fuel, (2) that the degree of corrosion of the steel specimens is directly related to the amount of exposure, and (3) that the phosphorizing of a fuel in accordance with the present invention greatly reduces the corrosiveness of the fuel ash.

Chemical analyses were made on the deposits that were formed or otherwise left on the steel specimens. The data obtained by these analyses are presented in the following table.

TABLE VI

| Fuel No. | Mol Ratio P/V in Fuel | Composition (Partial) of Deposits on Test Specimens | | | | | |
|---|---|---|---|---|---|---|---|
| | | Percent S | Percent V | Percent Na | Percent Mg | Percent Ca | Percent P |
| 359 | | | | | | | |
| 710 | 2.5/1 | | 7.12 | | | | 7.18 |
| 1230 | | <0.06 | 1.79 | 0.20 | <0.2 | | |
| 1288 | 4/1 | <0.02 | 6.73 | 2.02 | 0.43 | | 16.6 |

These results reveal that incorporation of phosphorus within the ash formed by the combustion of a vanadium-containing residual fuel may be satisfactorily and readily achieved by phosphorizing the fuel itself. The results furthermore show that a desirable P/V mol ratio (e. g. between 1/1 and 5/1) may be readily realized by employing P/V mol ratios of this same range in the fuel. Thus, in Table VI the P/V mol ratio in the deposits left by fuel 710 was about 1.7/1, and the ratio in the deposits left by fuel 1288 was about 4/1. The effectiveness of the phosphorus in these deposits in reducing the corrosiveness of the deposits was demonstrated previously in Table V.

In considering the data in Table VI, it will be appreciated that the results given do not total to 100%, since there were other constituents present that have not been included here. Thus, each deposit analyzed also contained one or more of the following elements: nickel, iron, oxygen, silicon, tin, cobalt, lead, aluminum, copper, chromium, silver, manganese and molybdenum.

If desired and under certain conditions of use it is preferred to incorporate alkaline earth metals in the compositions of this invention. The use of calcium and barium is particularly contemplated for this purpose. An alkaline earth metal may be incorporated in a fuel by (1) direct reaction of an alkaline earth metal compound with the fuel or (2) addition of an oil-soluble alkaline earth metal compound. Further, an alkaline earth metal may be incorporated in a residual fuel before, after, or simultaneously with the phosphorization of the fuel.

Suitable alkaline earth metal compounds for reaction directly with a residual fuel include the hydroxides or other bases of calcium and barium. Alkaline earth metal compounds suitable for addition to the residual fuel compositions described in this invention include oil-soluble alkaline earth metal salts of organic acids such as naphthenic or sulfonic acids and oil-soluble alkaline earth metal derivatives of the phosphorized organic compositions described earlier. Particularly desirable for addition to a residual fuel are the $P_2S_5$ or $P_2O_5$ treated alkaline earth metal compounds of alkylated phenol sulfides. Especially attractive are the $P_2S_5$ or $P_2O_5$ treated barium and calcium derivatives of alkylated phenol sulfides in which the alkyl group is a paraffinic group of normal, branched, or cycloparaffinic structure containing 5 to 22 carbon atoms and preferably 8 to 18 carbon atoms. An illustration of this type of compound is $P_2S_5$ treated barium iso-octyl phenol sulfide.

What is claimed is:

1. A residual fuel oil containing from 0.001 to 3.0 wt. percent of vanadium, expressed as $V_2O_5$, and an amount of a hydrocarbon-soluble, phosphorus-containing organic composition sufficient to provide from 1:1 to 5:1 mols of phosphorus per mol of vanadium within the fuel.



2. A residual fuel as defined in claim 1 in which the phosphorus to vanadium mol ratio is in the range of about 2.5:1 to 4:1.

3. A fuel composition comprising residual mineral oil hydrocarbons containing 0.001 to 3.0 wt. percent vanadium, expressed as $V_2O_5$, and an amount of an oil soluble phosphorus composition such that the ash produced by combustion of the fuel contains between 1 and 10 mols of phosphorus per mol of vanadium calculated as vanadium pentoxide.

4. A fuel composition comprising residual hydrocarbons containing 0.001 to 0.15 wt. percent vanadium, expressed as $V_2O_5$, and a proportion of an oil-soluble phosphorus-containing organic composition such that the ash produced by combustion of the fuel contains between 1 and 10 mols of phosphorus per mol of vanadium calculated as vanadium pentoxide.

5. A fuel composition comprising residual hydrocarbons containing from 0.001 to 3.0 wt. percent vanadium and an amount of an oil-soluble phosphorus-containing organic composition sufficient to render the ash formed by burning said fuel composition substantially non-corrosive toward ferrous metals, the amount of said phosphorus-containing composition being sufficient to provide the ash with between 1 and 5 mols of phosphorus per mol of vanadium.

6. A residual fuel containing amounts of vanadium such that the ash produced by combustion of the fuel is normally corrosive toward ferrous metals, and an amount of an added oil-soluble phosphorus composition sufficient to provide the ash with between 1 and 5 mols of phosphorus per mol of vanadium, whereby the said corrosive action of the ash is reduced.

7. A fuel oil as defined by claim 1 wherein said phosphorus-containing organic composition comprises reaction products obtained by treatment of petroleum components with a phosphorus compound selected from the group consisting of $P_2O_5$, $P_2S_5$ and orthophosphoric acid at temperatures in the range of about 100° F. to 500° F. for a period of about ½ to 8 hours.

8. A fuel oil as defined by claim 7 wherein said reaction products are obtained by treatment of a bright stock with $P_2S_5$.

9. A fuel oil as defined by claim 7 wherein said reaction products are obtained by treatment of residual fuel oil components with orthophosphoric acid.


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