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HIGH SULFUR CONTENT FUEL

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This invention relates to fuels which although having relatively high sulfur concentrations, are highly suitable for use in internal combustion engines, and particularly in diesel engines.

It has heretofore been observed that internal combustion engines, when operated on fuels having a relatively high sulfur content, exhibit much more corrosion on the metallic portions of the engine which contact the products of combustion of the fuel than when the sulfur content of the fuel is eliminated or substantially reduced; this is true irrespective of whether the sulfur is present in the free or combined state. This corrosion has been attributed to the acidic vapors formed on combustion of the sulfur-containing fuels, namely, sulfur dioxide and sulfur trioxide, and this is evidenced by the fact that the amount of corrosion increases with an increase in the sulfur content of the fuel. These gases, in the presence of water (which may be formed during fuel combustion and/or enter the engine through the air intake as the moisture normally present in the atmosphere), attack the metal parts exposed thereto. For example, corrosion is especially severe on the cylinder walls and piston rings since, at the pressures developed therein over at least a portion of the power stroke, the water is liquefied so that sulfur dioxide and trioxide dissolve therein to form sulfurous and/or sulfuric acid, which latter attack the exposed metal surfaces. The temperature of the cylinder also effects corrosion. Thus, engines operating at relatively low temperatures are more susceptible to corrosion since more moisture will condense at such lower temperatures. The thin oil film which may cover the metal parts affords only slight protection against the corrosive effects of the sulfur acids, which protection is completely inadequate whenever high sulfur content fuels are employed. However, the presence of sulfur in fuels has a beneficial effect in that the ignition properties of the fuel are improved thereby, i. e., fuel containing appreciable quantities of sulfur may be easily ignited in internal combustion engines.

A further disadvantage of employing high sulfur content fuels in internal combustion engines is that the sulfur products of combustion also attack the lubricating oil, and especially oil additives, i. e., materials added to the oil to impart special properties or characteristics thereto, such as materials which may be added to oils as pour point depressants, oiliness, color, extreme pressure and viscosity index improvers, and oxidation inhibitors. Another disadvantage of high

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sulfur content fuels is the formation of heavy piston deposits in diesel engines.

Recognition of the overall adverse effect of the presence of sulfur and sulfur-containing compounds in fuels for internal combustion engines has led to widespread use of various processes directed to the removal of sulfur, which may be accomplished with more or less success by methods known to the art. However, these processes at best are expensive, commonly produce worthless by-products, and frequently have an adverse effect on the fuel itself.

An object of the present invention is to eliminate the necessity of removing sulfur from fuels having a relatively high sulfur content. Another object is to provide a high sulfur content fuel composition which is substantially non-corrosive to the metal parts of internal combustion engines, and which does not cause excessive engine deposits. A further object is to provide a new method of operation for combustion engines. A still further object is to provide a novel process for the production of power from high sulfur content fuels. Other objects and their achievement according to the present invention will be apparent from the specification.

It has now been discovered that the incorporation of certain compounds, as hereinafter described, in high sulfur content fuels eliminates, or at least materially reduces, the corrosive effects caused by the presence of sulfur, and substantially decreases the formation of engine deposits, and thus the incorporation of these materials in fuels eliminates the necessity of treating such fuels for the removal of the sulfur therefrom.

According to the present invention, a small quantity of a metallic inorganic salt, as hereinafter defined, is incorporated in a high sulfur content fuel, it having been discovered that if such a material is incorporated into a fuel having a high sulfur content, the corrosive effects of the sulfur oxides are substantially reduced and even substantially completely eliminated.

By employing high sulfur content fuels containing incorporated therein only a relatively very small amount of a metallic inorganic salt, in accordance with the present invention, the corrosion of the metal parts is practically completely eliminated, or is substantially reduced, and engine deposits are reduced so that the corrosion and deposition is comparable to that observed with a fuel containing low or negligible quantities of sulfur, and hence the necessity for employing expensive processes for removing sulfur from fuels is obviated, and the advantages of having sulfur present to improve the ignition properties of the fuel are preserved. A further significant advantage of the present invention is the prevention of oil depletion, i. e., the oil and the oil additives are not attacked by the products of combustion of the fuel, and therefore the oil retains the original desired characteristics and special properties.

It is now evident that the present invention provides new fuel compositions, and a new method for operating combustion engines on high sulfur content fuels in a manner so that the influence of sulfur on wear and deposition is substantially eliminated. It is further evident that the present invention provides a novel process for the production of power by burning a high sulfur content fuel.

The advantages achieved by the present invention, however, are limited to the employment of high sulfur content fuels, since, as has been discovered, if the present inorganic salts be incorporated in fuels containing relatively small amounts of sulfur, below about 0.1%, no effect, either beneficial or adverse, is observed. By the expression "high sulfur content fuels," as used herein, is meant those fuels which contain sulfur, either in the free or combined state, to the extent of from about 0.1% to about 5.0% by weight, though even more sulfur may be present, and good results obtained therewith according to the present invention. By the term "fuel," as used herein, is meant the hydrocarbon fuels normally employed to actuate the various internal combustion engines, and which may contain the various usual additives. The present invention is particularly adapted for use in connection with fuels containing from about 0.2% to about 3% sulfur, since, when employing fuels containing sulfur within this range, the severe corrosion and deposition problems normally present are substantially obviated. By the term "sulfur," as used herein, is meant to include sulfur in both the free and combined states.

The metallic inorganic salts suitable for incorporation with the high sulfur content fuels, according to the present invention, are generally the metallic nitrates and carbonates. Preferred metallic elements are those of the alkali or alkaline earth groups, such as lithium, sodium, potassium, rubidium, cesium, calcium, strontium, and barium, though the salts of other base metals may be used, e. g., the salts of metals such as titanium, vanadium, chromium, magnesium, cobalt, nickel, copper, zinc, cadmium, mercury, aluminum, tin, lead, antimony and bismuth. By the term "base metal," as used herein, is meant those metals whose hydroxides are soluble in water, or the metals that oxidize rapidly as opposed to the noble metals. Thus, for example, the nitrates and carbonates of the alkali and alkaline earth metals, such as of sodium, potassium, magnesium, calcium and barium nitrates and carbonates illustrate a preferred group of inorganic salts for use in the present invention. Zinc nitrate and carbonate illustrate further preferred base metal salts. The nitrates are preferred.

The inorganic salts of the present invention may be incorporated in high sulfur content fuels by any convenient means. Some of the present salts, such as calcium nitrate, have been found to be sufficiently soluble in hydrocarbons, such as diesel fuels of high sulfur content, so that a sufficient quantity thereof may be dissolved directly therein to realize the advantages of the present invention, and this method of incorporating an inorganic salt, as herein defined, constitutes a preferred method of preparing the novel fuel compositions of the present invention. Where desirable, solutizers, such as isopropyl alcohol may be used to assist in the production of the fuel composition.

A further preferred embodiment of the present invention is the injection of a solution, suspension, or dispersion, preferably a solution, of the salt into the fuel or air stream during engine operation. For example, an alcoholic or aqueous solution of the salt may be injected into the engine intake air system, or into the fuel feed line prior to injection into the combustion chamber. Recourse may be had to a metering device to regulate the intermittent or continuous flow of the solution. When injection during engine operation is employed, the fuel compositions of the present invention are prepared at a point proximate to their ignition, which may be in the combustion chamber itself, and of course in such instances the fuel compositions have a finite but short life; the existence of the present fuel composition, in liquid, vaporized or atomized form, for any length of time prior to actual ignition thereof, is sufficient to result in the surprising advantages of the present invention.

While it is not desired to be limited by any theoretical explanation of the mechanism of the present invention whereby the presence of small amounts of the present metallic inorganic salts eliminates, or at least materially reduces, the corrosion and deposition in internal combustion engines normally observed when operated on high sulfur content fuels, it is believed that the herein described salts react with, or decompose under the conditions of combustion, or otherwise form materials which react with, the sulfur oxides or sulfur acids to form non-corrosive materials, which materials are expelled during the exhaust stroke instead of forming deposits. Thus, for example, an alkali metal nitrate may form the nitrite, or the oxide, which then reacts with sulfur trioxide and water (which is formed by the combustion and/or enters the combustion chamber with the intake air), or with sulfur trioxide per se, to form the non-corrosive metal sulfate. This reaction may occur while the reactants are in the gaseous phase, or on or in the oil film covering the various metal parts of the engine.

The following examples serve to illustrate the present invention, which is not to be considered as limited thereby.

Example 1

A standard Fairbanks Morse diesel engine was operated for 80 hours on a diesel fuel containing 0.7% sulfur, and the amount of ring wear determined. The experiment was repeated except that a solution of calcium nitrate in isopropyl alcohol was injected into the air intake system at the rate of 0.6 cc. per minute, the concentration of the injection solution being such that the fuel consumed contained 0.022% by weight of calcium nitrate (calculated as $Ca(NO_3)_2 \cdot 4H_2O$).

The use of calcium nitrate was found to reduce total ring wear by 50%. It was further observed that piston cleanliness was greatly improved when compared with the results obtained when the inorganic salt was not employed.

Example 2

The same diesel engine described in Example 1 was operated on a diesel fuel containing 0.7% sulfur, 0.022% by weight calcium nitrate (calculated as $Ca(NO_3)_2 \cdot 4H_2O$), and 1% by volume of isopropyl alcohol. Engine operation was for 80 hours.

The use of calcium nitrate blended directly in the high sulfur content fuel reduced ring wear by 33% as compared to ring wear observed with no fuel additive. Deposits on the piston skirt and in the ring belt area were practically eliminated.

Example 3

Example 2 was repeated except that the concentration of calcium nitrate was reduced to 0.0034% by weight (calculated as

$Ca(NO_3)_2 \cdot 4H_2O$)

Ring wear reduction over that observed when no fuel additive was employed was 11%.

Example 4

Example 2 was repeated except that 0.0315% by weight of zinc nitrate (calculated as

$Zn(NO_3)_2 \cdot 6H_2O$)

was incorporated in the fuel instead of calcium nitrate.

Ring wear reduction over that observed when no fuely additive was employed was 21%, and a substantial reduction of piston deposits was observed.

Example 5

A standard 1–71 General Motors diesel engine was operated for 80 hours on a diesel fuel containing 0.7% sulfur and the amount of ring wear and piston deposits determined. The experiment was repeated using the same fuel containing incorporated therein 0.022% by weight calcium nitrate (calculated as $Ca(NO_3)_2 \cdot 4H_2O$) and 1% by volume isopropyl alcohol.

Ring wear was reduced by 43% and piston deposits, particularly in the ring belt area, were substantially eliminated by the fuel additive.

Example 6

Example 5 was repeated except that

$Mg(NO_3)_2 \cdot 6H_2O$

in water solution was applied dropwise to the air induction system. $Mg(NO_3)_2 \cdot 6H_2O$ was calculated to be 0.038% of the total fuel used.

Ring wear was reduced by 38%, and engine cleanliness was improved, intake port deposits being reduced by 35%.

Example 7

Example 5 was repeated except that MgO as a powder was introduced into the intake air system in a quantity such that it constituted 0.013% of the fuel.

Ring wear was reduced by 30%, and engine cleanliness was improved, intake port deposits being reduced by 48%.

Example 8

Example 5 was repeated except that 0.015% of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.1% by volume of isopropyl alcohol was blended into 0.7% sulfur fuel, the resulting fuel composition being fed to the cylinders in the normal manner.

Ring wear was reduced by 21%, and engine cleanliness was improved, intake port deposits being reduced by 27%.

The optimum quantity of inorganic salt to be incorporated in the high sulfur content fuel will, of course, vary according to the quantity of sulfur in the fuel. As above stated, only very small quantities of the inorganic salts of the present invention need be added to the high sulfur content fuels in order to realize the advantages of the present invention. Thus, the preferred inorganic salts may be present in a quantity as low as about 0.003% by weight of the fuel, and corrosion will be substantially reduced. It is preferred, however, to employ from about 0.02% to about 0.5% by weight, though of course more may be employed where necessary or desirable.

As hereinbefore described and illustrated in the above examples, the incorporation of certain inorganic salts, as herein defined, in high sulfur content fuels reduces the corrosion attributable to the sulfur content so that the corrosion is comparable to that obtained with fuels containing only substantially negligible quantities of sulfur. The inorganic salts may also be introduced into the combustion chamber incorporated in the form of a solid suspension or dispersion in a wax or other viscous material. Other methods of simultaneously introducing metallic inorganic oxides and high sulfur content fuels into the combustion chamber will be apparent to those skilled in the art, for example, the injection of the salt without dilution, or injection in the form of emulsions, suspensions, dispersions, or solutions in various suitable materials. Other modifications of the present invention will also be apparent to those skilled in the art.

The foregoing discussion has been directed largely to diesel engine operation, but the present invention is also applicable to other internal combustion engines where the use of high sulfur content fuels causes corrosion problems, for example, in spark type internal combustion engines and in gas turbines.

The invention claimed is:

1. A high sulfur content diesel fuel which comprises a hydrocarbon diesel fuel containing from about 0.2% to about 3% sulfur, and from about 0.003% to about 0.5% by weight of hydrated calcium nitrate.

2. A high sulfur content fuel for internal combustion engines which comprises a hydrocarbon fuel containing from about 0.2% to about 3% sulfur and a minor amount sufficient to substantially reduce the engine wear caused by said sulfur of calcium nitrate.

3. A high sulfur content fuel for internal combustion engines which comprises a hydrocarbon fuel containing from about 0.2% to about 3% sulfur and a minor amount sufficient to substantially reduce the engine wear caused by said sulfur of an inorganic alkaline earth metal nitrate salt.

4. A high sulfur content fuel for internal combustion engines which comprises a hydrocarbon fuel containing from about 0.2% to about 3% sulfur and a minor amount sufficient to substantially reduce the engine wear caused by said sulfur of a hydrated inorganic alkaline earth metal nitrate salt.

5. A high sulfur content fuel for internal combustion engines which comprises a hydrocarbon diesel fuel containing at least about 0.2% sulfur and a minor amount greater than about 0.003 weight per cent and sufficient to substantially re-

duce the engine wear caused by said sulfur of a hydrated base metal inorganic nitrate.

6. The composition of claim 5 wherein the hydrated base metal inorganic nitrate is hydrated zinc nitrate.

7. The composition of claim 5 wherein the hydrated base metal inorganic nitrate is hydrated magnesium nitrate.

8. The composition of claim 5 wherein the sulfur content of the hydrocarbon diesel fuel is about 0.7 per cent.

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