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## FUEL FOR SPARK-IGNITION ENGINES

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The present invention relates to an improved liquid hydrocarbon fuel for spark-ignition internal combustion engines.

Petroleum refiners resort to extensive processing of crude oils in order to produce finished gasolines of high antiknock value. Still, it is nearly always necessary to add a knock suppressant to such gasolines. Lead tetraethyl (TEL) is at present universally employed for the purpose. This compound decomposes during the combustion of gasoline in the engine, and its lead recombines with certain elements present in the combustion chamber to form nonvolatile lead salts. A portion of these salts remains in the engine as a deposit on cylinder heads (walls of the combustion chamber), on piston tops and on exhaust valves.

Because the deposits formed on the exhaust valves shorten their life, deposit scavengers in the form of ethylene chloride and/or ethylene bromide are always added to gasoline, along the TEL. These scavengers cause formation of more volatile lead compounds, such as  $PbCl_2$  and  $PbBr_2$ , which evaporate from the hot exhaust valves and thus, by reducing the amount of deposits, prolong the valve life. Elsewhere in the combustion chamber the scavengers have little or no effect, because the temperatures prevailing there are too low to volatilize lead halides.

The lead also combines with two other elements always present during the combustion of the fuel in an engine—oxygen and sulfur, the result being formation of lead oxides and a large number of different lead salts, such as  $PbSO_4$ ,  $PbO \cdot PbSO_4$ ,  $2PbO \cdot PbCl_2$  and  $2PbO \cdot PbBr_2$ . In the total deposit, within the combustion chamber, from 85 to 98% by weight thereof may be composed of a mixture of such lead salts, the remainder being carbonaceous material formed in the combustion of the hydrocarbon fuel and/or lubricating oil.

The present day automotive spark-ignition engines have higher compression ratios than those of but a few years ago, are capable of greater power output, and have larger cylinder diameters. As a consequence of these increased compression ratios and greater power outputs, the average temperatures of combustion chamber surfaces in a running engine are higher than those which were normally obtained in the engines of the last decade. Furthermore, the larger cylinder diameters are responsible for a longer flame travel path and a longer exposure of the combustion chamber surfaces to the flame. Under these conditions, the mixture of lead salts and carbonaceous material in the deposit tends to ignite more readily and to glow longer than either the lead salts or the carbonaceous constituents alone. It was found that this is due to the catalytic effect of the lead salts on the burning of the carbonaceous material in the deposit, which effect tends to reduce the glow temperature of the carbonaceous material. While the minimum temperature at which pure carbon will glow lies in the range from about 1000 to about 1050° F., the presence of certain lead salts reduces the glow temperature of carbon by as much as 400° F.

The glowing of the carbonaceous material in the combustion chamber deposit, induced by the presence of lead salts, causes erratic ignition of the fuel-air mixture, as opposed to the normal ignition by the spark plugs. This erratic ignition is termed "surface-ignition" and can

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cause a very loud knock (so-called "wild ping"), a reduction in power, and, in extreme cases, may even lead to engine damage.

The combustion noise produced by surface-ignition is clearly distinguishable from detonation by its erratic character and, in general, cannot be suppressed by increasing octane number of fuel, either by refining methods or by adding TEL.

Not all lead compounds are alike in their ability to catalyze the burning of carbon. Some are virtually inert and thus would not reduce surface-ignition. Others, such as lead salts formed by combining with oxygen, sulfur and the halogens, are quite active in this respect.

I have now found that, by adding to the gasoline certain molybdenum compounds capable of converting the undesirable lead salts which promote surface-ignition to lead salts inactive in this respect, the occurrence of surface-ignition can be substantially reduced, if not totally suppressed.

More specifically, I have found that by introducing an effective concentration of a gasoline-soluble organomolybdenum compound into a hydrocarbon fuel boiling in the gasoline range and comprising conventional amounts of TEL antiknock additive, the occurrence of surface-ignition with all its attendant drawbacks can be unexpectedly and significantly reduced.

More specifically, I have found that, in employing gasolines having a Research octane number of the order of 90 and higher and containing from about 0.5 cc. of TEL to 3 cc. of TEL (the latter figure being the maximum employed in actual automotive practice), the addition of molybdenum in the form of a gasoline-soluble organomolybdenum compound, in a concentration from 0.1 theory to 3.0 theories of molybdenum, based on the total concentration of lead in the gasoline, will provide a substantial reduction of surface-ignition in the combustion chamber of a spark-ignition engine. One theory in this context refers to the amount of molybdenum necessary to convert all the lead to lead molybdate ( $PbMoO_4$ ). In general, the molybdenum-containing compound in amounts corresponding to from 0.2 to 1.0 theory of molybdenum will secure a satisfactorily substantial suppression, from about 50 to about 70% and more, of the surface-ignition.

While TEL is employed in the U.S. automotive practice as the anti-knock additive to gasoline in amounts not exceeding 3 cc. per gallon of gasoline, when, for any reason, more than 3 cc. per gallon of TEL is found to be permissible in the fuel, the introduction of the gasoline-soluble organomolybdenum compound into such leaded fuel in the aforementioned ranges of concentrations will similarly suppress occurrence of surface-ignition in the combustion chamber.

The present day gasolines, to a large extent, represent mixtures of hydrocarbons obtained by extensive refining of petroleum, which may involve thermal and/or catalytic cracking and thermal and/or catalytic reforming. These hydrocarbon mixtures, boiling in the gasoline range and intended for use as fuels in automotive spark-ignition engines, contain substantial proportions of  $C_8$  and heavier aromatic hydrocarbons, amounting to at least 15% and more commonly 20% by weight and more. At the same time, these modern gasoline fuels, when burning in the combustion chamber of an engine, are prone to produce larger quantities of carbonaceous deposits than the formerly used predominantly straight-run gasolines. As a consequence, the use of these newer gasolines containing the conventional TEL antiknock agent is more likely to be accompanied by surface-ignition.

The present invention, accordingly, by reducing the occurrence of this serious drawback of engine operation, permits of utilizing a larger variety of leaded fuels boil-

ing in the gasoline range, including those containing more than 15% by weight of  $C_8$  and heavier aromatic hydrocarbons.

As indicated hereinabove, the hydrocarbon fuels which can be employed in accordance with the present invention are mixtures of hydrocarbons boiling in the gasoline range, from an initial temperature of about 90° F. to a 90% point of about 400° F. and an end point of 440° F. (ASTM distillation D-86) and preferably having an aromatic content of more than 15% by weight. The clear Research octane rating of these fuels is above about 85, and the TEL content is as hereinbefore indicated.

A number of compounds of phosphorus have been proposed in the art to alleviate the drawbacks of surface-ignition in spark-ignition engines. Such compounds include, among others, organic phosphates, specifically tricresyl phosphate (TCP); trialkyl phosphines, specifically tri-n-butyl phosphine (TAP); thionophosphates, specifically chloropropyl thionophosphate (ICC). The symbols TCP, TAP and ICC are those used to designate these additives by the trade. Although generally effective insofar as the reduction of surface-ignition is concerned, these phosphorus-containing additives are prone to bring about certain side-effects, such as lowering of octane number, tendency of exhaust valves to burn out prematurely, increased engine varnish, increased intake-port and intake-valve deposits, and increased octane requirement of the engine. In view of the possible occurrences of these several side-effects, only small amounts of phosphorus-containing additives, such as TCP or ICC, of the order of 0.4 theory, have been preferably employed in gasolines containing up to 3 cc. of TEL per each gallon of the gasoline.

It is now found that these phosphorus-containing additives, such as TCP, are compatible with the organo-molybdenum surface-ignition suppressants of the present invention and, when combined therewith in leaded gasoline, contribute their desirable surface-ignition suppressing action to the like action of the organo-molybdenum suppressants.

The spark-ignition internal combustion engines in which the improved fuels of this invention can be advantageously employed are those with compression ratios from 7:1, preferably from 8.5:1 through 11:1, and upward. The organo-molybdenum compounds, added to the fuel as the surface-ignition suppressants, may be introduced into the fuel at any stage following its recovery at the refinery and prior to its use in the engine. They can be introduced into the gasoline in the form of a carbonyl, a chelate, a cyclopentadienyl, or any other suitable organo-molybdenum compound soluble in gasoline. As illustrative examples of such molybdenum-containing additives, the following may be mentioned: molybdenum hexacarbonyl; bis-(octylene glycol)-molybdate; 2,3-hexane diol molybdate; bis-(cyclopentadienyl)-m-pentacarbonmonoxide-bi-molybdenum; tridecyl molybdate, etc.

The effectiveness of the gasoline fuels employed in accordance with the present invention has been established in a series of laboratory engine tests. These tests were carried out in a single cylinder L-head CFR engine, of the kind described for instance by Hirschler et al. on pages 44-45 of vol. 62 of SAE Transactions for 1954. The engine was run at full throttle at a steady rate of 900 r.p.m. with the jacket temperature being maintained at 150° F. Polypropylene glycol phenyl methyl diether of an average molecular weight of about 1000 was employed as the crankcase lubricant. The crankcase temperature of the lubricant was 140° F. The air/fuel ratio employed in this test series was 13:1. As a base fuel there was employed a catalytically cracked hydrocarbon stock (10% boiling point, at 135° F.; 50%, at about 275° F.; 90%, at about 380° F.; end point at 400° F.). This fuel contained the conventional TEL motor mix (3 cc./gal. TEL and, as scavengers, 1 theory of ethylene chloride and ½ theory of ethylene bromide). The engine head was provided with a single spark plug, and a

pressure-recording device in the form of a known magnetostrictive indicator which transmitted pressure pulses to a thyratron-operated counting circuit.

The following examples of the comparative data from these test series, obtained in 100 hour runs, illustrate reduction of the surface-ignition and thus indicate the improvement in combustion performance achieved through the application of the fuel compositions prepared in accordance with the present invention.

#### *Runs with leaded base fuel*

In four runs with the base fuel containing the conventional TEL motor mix the average number of counts per hour observed in running the engine for 100 hours was equal to 425. The engine was disassembled upon completion of each run, and the combustion chamber and exhaust valve deposits were scraped off, weighed and analyzed by X-ray diffraction and X-ray absorption techniques. The major proportion (more than 50% by volume) of the lead in the deposit collected from the walls of the combustion chamber consisted of lead halides. The lead in the deposit collected from the exhaust valve was mainly in the form of lead sulfate and oxysulfate.

#### *Runs with base fuel containing organo-molybdenum additives*

*Run (a).*—One theory of molybdenum, in the form of molybdenum hexacarbonyl, was employed as the surface-ignition suppressant in this run. Surface-ignition occurred at a rate of 126 counts per hour. In other words, it was reduced to 30% of the figure observed in the runs with leaded base fuel alone. The X-ray diffraction and absorption analyses of the deposits scraped from the interior of the combustion chamber and the exhaust valves showed that the lead in the deposit was present almost entirely in the form of  $PbMoO_4$ .

*Run (b).*—0.2 theory of molybdenum as molybdenum hexacarbonyl was employed in this run. Surface-ignition observations indicated a rate of 200 counts per hour corresponding to a reduction of 53%, as compared to the surface-ignition observed with the leaded base fuel alone. The X-ray diffraction and absorption analyses of the deposits scraped from the combustion chamber walls and from the exhaust valves disclosed that at least 25% by volume of the lead in the deposit was present as lead molybdate.

*Run (c).*—In this run 0.3 theory of the same organo-molybdenum additive as in Runs (a) and (b) and 0.1 theory of tricresyl phosphate were added to the "leaded" base fuel. Surface-ignition was reduced to 37% of the figure observed in parallel 100 hour runs with the leaded base fuel alone, as indicated by a rate of 155 counts per hour. As much as 40% of lead molybdate was found to be present in the deposits by X-ray diffraction and absorption analyses.

*Run (d).*—In this run, 0.1 theory of the same organo-molybdenum surface-ignition suppressant and 0.3 theory of tricresyl phosphate were added to the fuel. Surface-ignition observed was 34% of that recorded in similar 100 hour runs with unmodified leaded base fuel, as indicated by a rate of 146 counts per hour. X-ray diffraction and adsorption analyses indicated the presence of about 15% of lead molybdate in the deposit.

Although the actual theory underlying the reduction of surface-ignition upon addition of an organo-molybdenum compound to a leaded gasoline in accordance with the invention is not fully understood, it is surmised that this reduction is based on the conversion to lead molybdate ( $PbMoO_4$ ) of at least a substantial proportion (10 to 15 volume percent and higher) of the lead present in the deposit in the form of various salts; bromides, oxybromides, chlorides, oxychlorides, sulfates, oxysulfates, etc. Lead molybdate has a much lower tendency to catalyze carbon burning than the aforementioned halides and sulfates, and therefore, its presence in the deposit

minimizes occurrences of "hot spots," thus reducing the surface-ignition.

A special test procedure developed to ascertain the glow temperatures of different lead salts alone and admixed with carbon, and representative samples of deposits formed by lead salts and carbonaceous material, when tested by this procedure, appeared to bear out this hypothesis. The procedure consisted in heating a cylindrical pellet ( $\frac{1}{4} \times \frac{1}{4}$ ") shaped from the deposit in a furnace at a selected temperature. Nitrogen was passed through the furnace for two minutes, while the pellet came to temperature, whereupon air was introduced. If the pellet became incandescent within two minutes after the introduction of air, another pellet was tested at a lower temperature. On the other hand, if the first pellet failed to glow, another similar pellet was subjected to a higher temperature. Temperature intervals of 18° F. were employed, bracketing the range of "glow temperature." This latter term designated the temperature at which a pellet would not glow, but such that glowing would initiate 18° F. above it.

The tendency of the materials to persist in glowing was checked by igniting a pellet directly in the flame of a Bunsen burner, removing the flame and observing duration of the glow.

By employing these testing techniques it was found that the glow temperature of pure carbon lies in the range from 1004 to 1040° F., the carbon pellet displaying substantially no tendency to persist in glowing. The glow temperature of lead oxide (using a pellet containing 90% PbO and 10% carbon) was found to range from 734° to 770° F. For a similar pellet with the proportions of PbO and carbon reversed (10% and 90%), the glow temperature ranged from 824° to 860° F., and the glow lasted at least 15 seconds after the flame was withdrawn. Deposits containing various lead salts, such as lead oxysulfate, lead oxybromide, lead oxychloride, etc., had glow temperatures of less than 600° F. for pellets containing 90% lead salt and 10% carbon, and below 770° for pellets containing 10% lead salt and 90% carbon. Contrasted therewith pellets containing 90% lead molybdate and 10% carbon had glow temperatures in the range from 1004° to 1022° F., while pellets containing 10% lead molybdate and 90% carbon had glow temperatures from about 896° to 932° F.

In any event, whatever be the exact theoretical explanation of the effectiveness of organo-molybdenum additives as surface-ignition suppressants, a substantial reduction of at least 50%, and more, of the surface-ignition is invariably achieved by the addition of gasoline-soluble organo-molybdenum compounds to leaded gasolines in accordance with the invention.

While the invention is described hereinabove with reference to certain specific illustrative examples, it will be obvious to the readers that it is not limited by the details of such examples, except as hereinafter defined in the appended claims. It is to be understood that the invention is not to be limited to the use of isolated specific organo-molybdenum compounds employed in the aforementioned examples to illustrate the operativeness of the invention. On the contrary, the invention contemplates the use of all gasoline-soluble organo-molybdenum compounds capable, whether alone or in combination with compatible organo-phosphorus compounds, to effect a substantial reduction of surface-ignition in the combustion of leaded hydrocarbon fuels boiling in the gasoline range in spark-ignition internal combustion engines.

It will be furthermore understood that the invention is not limited to leaded gasolines containing surface-ignition suppressing organo-molybdenum materials as the only additives thereto. Other known additives, for in-

stance, gum inhibitors, rust inhibitors, deicing agents, dyes, etc., may be added for the purpose of enhancing various qualities of loaded gasolines provided these additives are employed in conventional amounts, are compatible with the molybdenum-containing surface-ignition suppressants of this invention, and do not detract from the desirable action thereof.

I claim:

1. An improved fuel for use in a spark-ignition internal combustion engine, said fuel consisting essentially of, as the predominant component, leaded gasoline having a clear octane number above about 85, and, as a surface-ignition suppressant, the combination of from 0.1 to 3.0 theories of molybdenum hexacarbonyl and from 0.1 to 0.4 theory of an organo-phosphorus compound.

2. An improved fuel as defined in claim 1, in which said leaded gasoline has an aromatic hydrocarbon content of at least 20% by weight.

3. An improved fuel for use in a spark-ignition internal combustion engine, such fuel consisting essentially of, as the predominant component, leaded gasoline having a clear octane number above about 85, and, as a surface-ignition suppressant, the combination of from 0.1 to 3.0 theories of molybdenum hexacarbonyl and from 0.1 to 0.4 theory of tricresyl phosphate.

4. An improved fuel as defined in claim 3, in which said leaded gasoline has an aromatic hydrocarbon content of at least 20% by weight.

5. A spark-ignition internal combustion engine fuel composition consisting essentially of petroleum hydrocarbons boiling within the gasoline boiling range and having an octane number when clear of at least about 85, containing a minor antiknock amount of a tetraalkyl lead and molybdenum hexacarbonyl in a small amount equivalent to about 0.070 to 0.150 gram of elemental molybdenum per gallon.

6. The method of reducing surface-ignition in a spark-ignition internal combustion engine, which comprises burning in the engine a hydrocarbon fuel consisting essentially of leaded gasoline having a clear octane number above about 85 and, as a surface-ignition suppressant, the combination of from 0.1 to 3.0 theories of a gasoline-soluble molybdenum hexacarbonyl and from 0.1 to 0.4 theory of an organo-phosphorus compound.

7. A method of reducing surface-ignition in a spark-ignition internal combustion engine, which comprises burning in the engine a hydrocarbon fuel consisting essentially of leaded gasoline having a clear octane number above about 85 and, as a surface-ignition suppressant, the combination of from 0.1 to 3.0 theories of a gasoline-soluble molybdenum hexacarbonyl and from 0.1 to 0.4 theory of tricresyl phosphate.

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