PATENT SPECIFICATION

776,189

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COMPLETE SPECIFICATION

Improved fuel composition

We, CALIFORNIA RESEARCH CORPORATION, a corporation duly organized under the laws of the State of Delaware, United States of America, of 200 Bush Street, San Francisco 4, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved fuels for compression ignition engines and more particularly to fuels for compression ignition engines containing additives which substantially reduce deposition and wear incident to the combustion of the fuel.

With the increased application of compression ignition engines, such as Diesel engines, in the field of transportation and power production, greater emphasis has been placed upon improvements in the operating efficiencies of the engine as effected by the fuel compound. It has been recognized that a number of undesirable features in Diesel engine operation, such as increased fuel consumption, excessive exhaust smoking, and certain facets of engine overhauling due to wear, may be in part attributed to the fuel oil and is particularly a function of the deposit-forming characteristics of the fuel oil.

It has been determined that the presence of deposits on the fuel injector tips alters the normal fuel spray pattern and results in inefficient engine operation due to incomplete fuel combustion. The resulting incomplete combustion of the fuel, occasioned by the presence of deposits in the fuel injection system and the combustion zone, increases the fuel consumption and promotes exhaust smoking, which is particularly objectionable in Diesel trucking operations.

Recently, it has been noted that Diesel fuels containing relatively large amounts of sulfur have been marketed extensively. It has been recognized that the presence of sulfur contributes to the formation of a corrosive combustion product which in turn promotes engine wear. In order to offset the corrosive action attributed to the presence of sulfur in Diesel fuel, it has been previously proposed to incorporate an organic metal oxide compound in the high-sulfur Diesel fuel. However, such proposal, while of merit in reducing the corrosive effect of the sulfur in the fuel, imparts additional objectionable features and increases the deposit-forming characteristics of the fuel oil.

Specification No. 674,765 discloses an anti-clogging concentrate comprising a hydrocarbon fuel oil containing a basic polyvalent metal salt of an organic acidic compound or a mixture of such salts, and a non-clogging hydrocarbon fuel oil comprising a hydrocarbon fuel oil containing not more than 0.03% by weight of the salt or mixture. The fuel oils boil in a range of from 340 to 700°F, and preferably of 400 to 675°F. The basic salts have the formula $(RY)n\ M\ (XH)m$ in which n and m are integers the sum of which equals the valency of the polyvalent metal M: X is O, S, Se or Te; R is an organic radical; and Y is an acidic group such as —CXX—, —X—, $—SO_3—$, $—SO_4—$ or PX_4. The salts include basic lead naphthenate and calcium petroleum sulphonate.

Sludge-preventing detergents may be added to the treated fuels or concentrates. These detergents are alkali, alkaline earth and heavy metal and organic nitrogen base salts of various organic acids, other than basic polyvalent metal salts of organic acids and include normal lead napthenates and calcium sulphonates.

The concentrate generally contains 2-25% of the basic salt and 0-15% of the detergent, and the fuel generally comprises from 0.001

[*Price* 3*s*. 6*d*.]

to 0.0125 of the basic salt and up to 0.0075% of the detergent.

Specification No. 685,117 discloses an anti-clogging concentrate comprising a cracked hydrocarbon fuel oil containing a salt of an organic alicyclic acid (or mixture of such salts) and a detergent, and a non-clogging cracked hydrocarbon fuel oil in which the oil contains not more than 0.025% by weight of the salt (or mixture) and not more than 0.02% by weight of a detergent.

The fuel oils boil in a range of from 300 to 750°F, and preferably from 400 to 675°F, the salts include lead petroleum naphthenates, and the detergents include calcium petroleum sulphonates. The concentrate includes 10-20% of the salt or salts and 5-15% of the detergent whilst the, treated fuels comprise 0.005-0.01% of the salt or salts and 0.0025-0.0075% of the detergent.

It has now been found that deposition and wear incident to the combustion of fuel oil boiling from 350 to 850°F can be materially reduced by incorporating in a hydrocarbon fuel a particular mixture of metal salts when mixed in a critical ratio. According to the invention there is provided an improved fuel comprising a major proportion of hydrocarbons boiling within the range of 350°F. to 850°F., and a mixture of an oil-soluble calcium mahogany sulfonate and an oil-soluble lead petroleum naphthenate, in a minor proportion of at least 0.3 mg atoms of metal per kg of fuel, wherein the mole ratio of the calcium sulfonate to the lead naphthenate varies from 1:70 to 1:1. This synergistic additive mixture materially reduces the deposit-forming propensities of a Diesel fuel, while at the same time reducing wear associated with the presence of sulfur in the hydrocarbon fuel. The improvement is applicable to a low-sulfur as well as to a high-sulfur Diesel fuel.

While the additive mixture may be incorporated in any hydrocarbon fuel boiling in the range of 350 to 850°F. suitable for use in internal combustion engines and particularly Diesel engines, the improving effect of the additive is particularly found in those hydrocarbon fuels containing above about 0.5 weight percent of sulfur. Ordinarily, the base fuels are a mixture of hydrocarbons derived from various petroleum crude oils. However, hydrocarbon fuels derived from other sources, such as shale oil, or synthetic hydrocarbons obtained from the Fischer-Tropsch process, may be improved by the invention. Specific examples of high-sulfur base fuels are those derived from West Texas crudes, Santa Maria crudes or the Arabian crudes, and involve either straight-run distillates or cracked distillates employed per se or as blends.

As previously mentioned, the additive comprises a critical mixture of an oil-soluble calcium mahogany sulfonate and an oil-soluble lead petroleum naphthenate. Sulfonic acids having a molecular weight of from 300 to 800 have been found suitable, although it is preferred to employ sulfonic acids having molecular weights above 400. The hydrocarbon radical of the sulfonic acid should be of sufficient molecular weight to impart oil solubility to the compound. The calcium salt of the sulfonic acid may be either neutral or basic, provided the resulting compound is sufficiently oil-soluble to maintain a stable dispersion in the hydrocarbon fuel when employed in the desired concentration.

The second component of the additive mixture is the lead soap of a petroleum naphthenic acid. These acids are generally obtained as a mixture of alicyclic carboxylic acids whose average molecular weight will vary depending upon the crude source and the fraction of petroleum oil from which the acids are obtained. The acids generally contain a 5 carbon atom alicyclic ring which is substituted by alkyl radicals, and the carboxyl group is usually on the beta carbon of the ring. Generally suitable for the purposes of the invention are those petroleum naphthenic acids having molecular weights above about 225. The lead salt may be present as the neutral or basic salt, as well as mixtures thereof.

From the minimum concentration of 0.3 mg atoms of metal per kg of fuel the amount of additive incorporated into the fuel may be varied, depending upon the type of base fuel and the degree of improvement desired. The specific concentration will generally be within the range of 0.3 to 3.0 milligram atoms of metal per kilogram of fuel. For optimum effectiveness of the additive, it has been found preferable to incorporate the additive at a concentration between 0.5 and 2.0 milligram atoms of metal per kilogram of fuel. For optimum effectiveness, the mol ratio range of calcium sulfonate to lead naphthenate will preferably lie within the range of about 1:40 to about 1:4 and, on the basis of the percent concentration of calcium sulfonate, from about 3 to 25% of the additive combination.

While all reference heretofore has been with respect to the direct incorporation of the additive in a hydrocarbon base fuel, it is to be understood that it is also contemplated that an additive concentrate may be prepared for incorporation into conventional Diesel fuels in the field. Such additive concentrate will contain the oil-soluble calcium mahogany sulfonate and the oil-soluble lead petroleum naphthenate in the molecular ratio range of from 1:70 to 1:1, and is dissolved in a hydrocarbon solvent carrier, preferably to the extent of its solubility.

The solvent carrier may contain hydrocarbons boiling in the Diesel fuel boiling range or mixtures thereof with lower boiling hydrocarbons which may be necessary to increase the solubility and maintain the high concentration of additive. Depending upon the particular type of hydrocarbon solvent employed as the carrier, a concentrate may be obtained which contains from 30 to 50% by weight of the additive combination. In application, this concentrate is then incorporated in the base fuel to be improved in such proportions as to result in a final concentration of at least 0.3, and preferably 0.3 to 3.0 milligram atoms of metal, per kilogram of fuel.

As an illustration of the effectiveness of the additive in the improvement of compression ignition engines, the following examples are presented. In these examples, a calcium mahogany sulfonate was employed in which the sulfonic acid possessed a molecular weight in the range of 480 to 505. The sulfonic acid was obtained by sulfonation with fuming sulfuric acid having a 20% content of SO_3 of a solvent-refined neutral distillate with an SSU at 100°F. of 480 to 500. The calcium salt was prepared by metathesis with the sodium salt and contained about 5 to 8% of free calcium hydroxide. The lead petroleum naphthenate used was a conventional 60% basic lead salt of naphthenic acids derived from a Midway crude oil and having an average molecular weight of 230. The range of molecular weight of the acids in the mixture of alicyclic carboxylic acids was from 200 to 260.

EXAMPLE I

This example is presented to illustrate the criticality in the sulfonate-naphthenate mol ratio on deposit formation, particularly with respect to the ring belt area of the pistons. As will be appreciated, extensive piston ring grooves deposition causes ring sticking which latter, in turn, causes "blow-by" and cylinder galling.

In these tests, the fuel employed was a straight-run distillate fuel with an API gravity of 33°, a cetane number of 44, and a sulfur content of 0.75%. The ASTM D-158 distillation of the fuel was as follows: start—350°F.; 10%—437°F.; 50%—529°F.; 90%—612°F.; end point—666°F. The total quantity of metals in the additive mixture added to the base fuel amounted to 1.3 milligram atoms of metal per kilogram of fuel. The fuels containing varying concentrations of calcium mahogany sulfonate and lead petroleum naphthenate were tested in a Caterpillar Diesel engine having a 4¼-inch piston bore according to conventional procedure under the following operating conditions:

Test time	120 hours
Speed RPM	1400
Load, percent of rated	100
Jacket temperature °F.	175
Oil sump temperature °F.	150
Intake air temperature °F.	110

In evaluating the performance of the respective test fuels at the conclusion of the test periods, the engine was dismantled and the pistons were examined and evaluated in accordance with the evaluation procedure disclosed in "Progress Report on Full-Scale Field Service Tests of Railroad Diesel Fuels," Coordinating Research Council (August, 1953), pages 80-83. In this evaluation, the ring groove deposit number (GD number) involves an estimate of the volume of deposit in the bottom of the ring grooves over the entire circumference. Values for thickness, width and circumferential lengths are assigned as follows:—

Thickness

Light brown to brown lacquer	0.5
Dark brown to heavy black laquer	1.0
Groove completely filled to ring bottom	10.0

Width

One-fourth of ring groove width	0.25
One-half of ring groove width	0.50
Three-quarters of ring groove width	0.75
Full ring groove width	1.0

Circumference

36° (1/10 total circumference)	1.0
90°	2.5
180°	5.0
270°	7.5
360° (full circumference)	10.0

The separate segment evaluations of thickness, width and circumference are multiplied together to give the product, and the sum of the individual products is designated as the ring groove deposit number or GD number. According to this method of evaluation, a ring groove completely filled to the back surface of the piston ring would have a GD number of 100; the groove covered with black lacquer would have a GD number of 10; and a completely clean groove would have a GD number of O.

The method of evaluating the piston land deposits involves an estimate of the percentage of the land area covered with black, dark grey or brown, grey or brown, or light grey or brown deposits. Numbers 8, 6, 4, and 2, respectively, are used in calculating the numerical piston discoloration number or PD number. The darkness of the deposit is indicative of the thickness, and a heavy black deposit is, in many cases, the forerunner of seizure. The range of possible PD number is from O in the case of a clean land area to 100×8 or 800 on a completely black land area.

The results obtained from a series of engine tests employing varying concentrations of lead naphthenate and calcium sulfonate are graphically presented in Figures 1 and 2 of the accompanying drawings. These data clearly indicate the unexpected synergistic result when employing the additive within the critical mol ratio range of from 1:70 to 1:1 of the combination of calcium sulfonate and lead naphthenate and particularly when the calcium sulfonate content of the additive is within the range of 1.4 to 50%.

EXAMPLE II

As an indication of the improved combustion characteristics of a fuel containing the additive within the critical mol ratio range, the following test results are presented. In these experiments, the test fuels are subjected to engine operating conditions which are the most conducive to high fuel consumption and deposit formation as evidenced by exhaust smoking. The test was conducted on a GM single-cylinder engine (GM 1-71), operated under the following conditions:

Rated load, per cent.	10
Engine RPM	1200
Test duration, hours	200
Jacket temperature °F.	170
Oil sump temperature °F.	180

The exhaust smoke measurements were obtained with a modified CRC photovolt smoke meter which consisted of a 2-inch diameter tube, 6 inches long, fitted with glass windows at each end. A light source was mounted at one end and a photocell connected to a microammeter graduated in percent smoke on the other end. A blower and a system of valves were provided for either introducing an exhaust sample into the tube or for scavenging the tube with clean air. In operation, the light intensity was adjusted to give full scale deflection (0 smoke) on the microammeter when the tube was free of smoke. Upon introduction of the exhaust sample into the tube, the meter deflection dropped off in proportion to the smoke density, but the meter reading as percent smoke increased. 100% smoke is arbitrarily defined as that amount of smoke which will just extinguish all the light impinging on the photocell; in this case, the meter deflection is 0. Contrary-wise, a meter deflection of 100 comprises 100% light transmission or no smoke in the tube.

In these experiments the base fuel was a straight-run distillate fuel having an API gravity of 33°, a cetane number of 44, a sulfur content of 0.75% and the following ASTM D-158 distillation: start—350°F.; 10%—437°F.; 50%—529°F.; 90%—612°F.; end point—666°F. To this base fuel was incorporated 0.65 millimols per kilogram of lead petroleum naphthenate and 0.04 millimols per kilogram of calcium mahogany sulfonate.

The results obtained from these tests are graphically represented in Figure 3 of the accompanying drawings. The erratic behavior of the smoke meter readings on the base fuel indicate a characteristic build-up and breaking-off of deposits on the tip of the fuel injector, while the fuel containing the additive continuously inhibits the formation of deposits and maintains the combustion system in efficient operation even under the rigorous conditions of the test.

In separate experiments, it has been observed that lead naphthenate per se, when incorporated in a comparable fuel base, will materially increase deposit formation over the base fuel as evidenced by the increase in exhaust smoking.

What we claim is:—

1. An improved fuel comprising a major proportion of hydrocarbons boiling within the range of 350°F. to 850°F., and a mixture of an oil-soluble calcium mahogany sulfonate and an oil-soluble lead petroleum naphthenate, said mixture being present in a minor proportion of at least 0.3 mg atoms of metal per kg of fuel, wherein the mole ratio of the sulfonate to the naphthenate is in a range of from 1:70 to 1:1.

2. A fuel as claimed in claim 1, wherein the sulfonate and naphthenate are present in amounts corresponding to a total of 0.3 to 3.0 milligram atoms of metal per kilogram of fuel.

3. A concentrate adapted to be added to Diesel fuel oil to reduce deposition and wear incident to the combustion of said fuel, comprising from 30 to 50% by weight of a mixture of an oil soluble calcium mahogany sulfonate and an oil-soluble lead petroleum naphthenate, wherein the mole ratio of the sulphonate to the naphthenate is in a range of from 1:70 to 1:1.

4. An improved fuel, substantially as hereinbefore described with reference to Example 1 or 2 and the accompanying drawings.

Dated this 23rd day of November, 1954.

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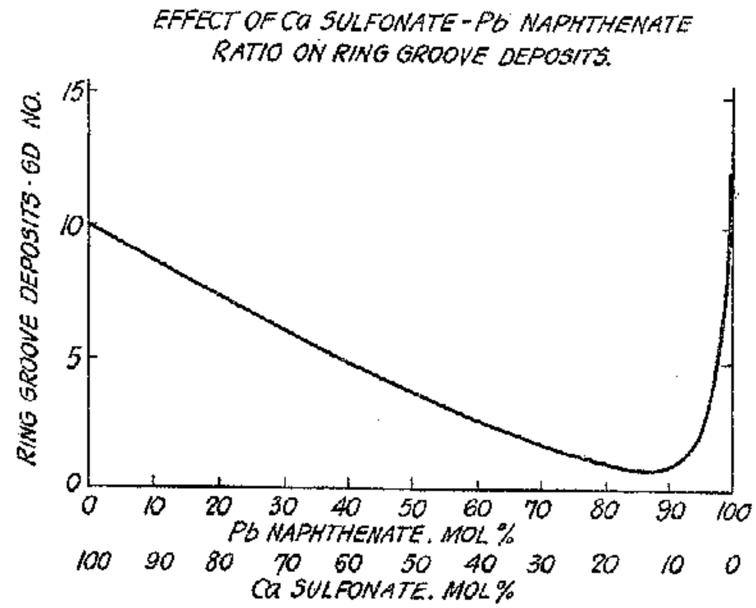
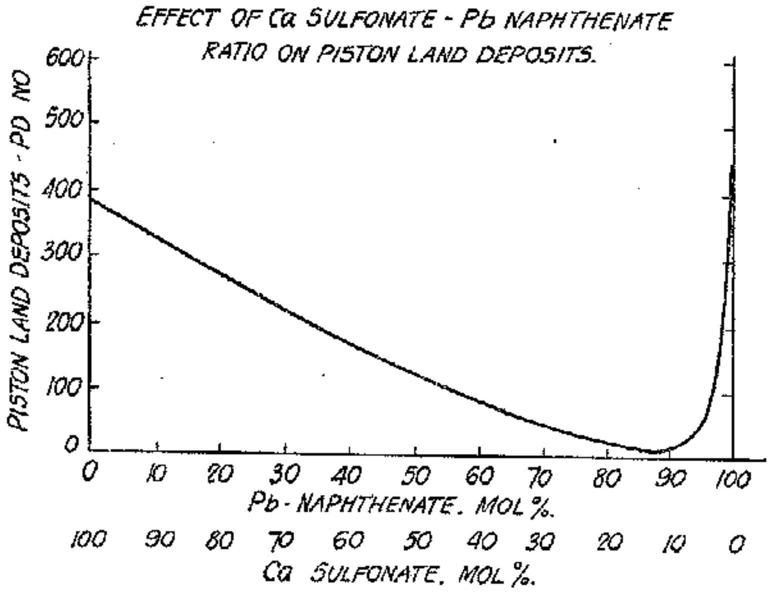
776,189 COMPLETE SPECIFICATION
2 SHEETS

This drawing is a reproduction of the Original on a reduced scale.
SHEET 1

FIG.1.



EFFECT OF Ca SULFONATE - Pb NAPHTHENATE RATIO ON RING GROOVE DEPOSITS.



EFFECT OF Ca SULFONATE - Pb NAPHTHENATE RATIO ON PISTON LAND DEPOSITS.

FIG. 2.

776,189 **COMPLETE SPECIFICATION**
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale.*
SHEET 2

FIG. 3.

EFFECT OF Ca SULFONATE - Pb NAPHTHENATE MIXTURE ON ENGINE PERFORMANCE