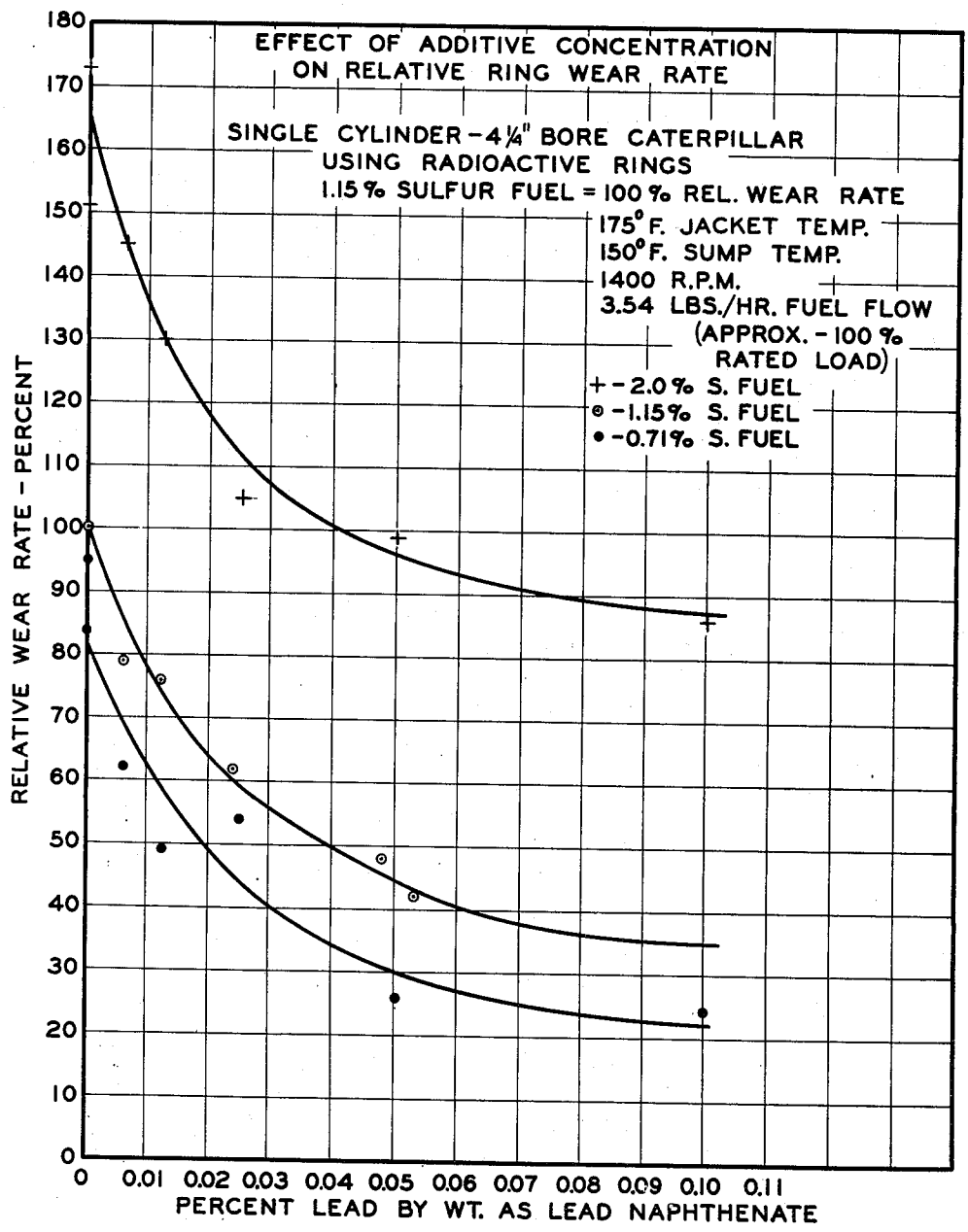
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HIGH SULFUR DIESEL FUEL CONTAINING ORGANIC LEAD SALTS

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HIGH SULFUR DIESEL FUEL CONTAINING ORGANIC LEAD SALTS

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1

This invention relates to a fuel for use in compression ignition engines, in particular to a diesel fuel consisting essentially of a petroleum distillate characterized by a high sulfur content above about 0.5% by weight and especially above 1.0% by weight and by a boiling range lying within the temperature range about 350–750° F., and a minor amount of an oil-soluble lead compound selected from the group consisting of lead naphthenates and lead sulfonates, sufficient to substantially decrease the engine wear incident to the combustion of the fuel.

It is recognized in the literature that engine wear rates are increased markedly as the sulfur content of the fuel rises. This increase in wear is attributed to the corrosive action of the combustion products of the sulfur compounds contained in the fuel on the interior metallic surfaces of the engine. Recognition of this effect of sulfur compounds in the fuel has led to the setting up of fairly rigid specifications in respect to sulfur content in diesel fuels. For example, in ASTM Standards on Petroleum Products and Lubricants, November 1948, published by the American Society for Testing Materials, tentative specifications for diesel fuel oils are set out at pages 548 and 549. For a volatile distillate fuel oil for engines in service requiring frequent speed and load changes such as an automotive diesel engine a maximum sulfur content of 0.50% by weight is specified. For distillate fuels of low volatility for engines in industrial and heavy mobile service a maximum sulfur content of 1.0% is specified. In the appended comments on the standards set out in the ASTM specifications for diesel fuels it is stated that the effect of sulfur content on engine wear appears to vary considerably in importance depending on engine design and operating conditions, and that in order to make available the widest range of fuels the permissible sulfur contents were specified at as high a value as practicable. Various manufacturers of diesel engines supply their customers with recommended fuel specifications. These recommendations include such specifications as a maximum sulfur content of 0.25% for diesel fuels for winter use in high speed automotive engines and a maximum sulfur content of 1% for some railroad diesel engines.

In consequence of the established effect of sulfur compounds in diesel fuels on engine wear and the various relatively low maximum sulfur contents which have been recommended for diesel fuels, petroleum refiners have been forced to market large volumes of diesel fuels having

2

low sulfur content, for example, well below 0.5% by weight. In order to meet these specifications, many stocks must be either treated at considerable expense to reduce sulfur content or their use in diesel fuel must be avoided. During the past several years the ratio of high sulfur crude oil refined to total crude oil refined has very markedly increased. This trend, coupled with the fairly rigid diesel fuel specifications for sulfur, presents the petroleum refiner with a serious problem of determining how high-sulfur, middle-of-the-barrel fractions may be economically utilized.

It is the paramount object of this invention to provide a diesel engine fuel composition in which high sulfur petroleum distillates may be used without first subjecting them to expensive desulfurization processes.

It is a further object of this invention to provide a diesel fuel having a high sulfur content which may be burned in internal combustion engines without producing the high engine wear rates which are ordinarily observed when high sulfur fuels are burned.

It has been found that the addition of a minor amount of an oil-soluble lead salt of an organic acid or of an organo-inorganic acid to a petroleum distillate boiling in the boiling range of diesel fuels and having a high sulfur content such as above 0.5% by weight or especially above 1.0% by weight produces very marked reductions in engine wear when the fuel containing the lead compound is burned.

The marked reduction in engine wear observed when lead naphthenates are introduced into the fuel is not accompanied by any increase in engine deposits even though no lead scavenger is used. This is rather unexpected in the light of past experience with spark ignition engines in which gasoline containing tetraethyl lead has been burned. The gasoline experience has been that no appreciable alteration in wear rate is observed by the addition of tetraethyl lead alone and that engine deposits are noticeably increased. To offset the engine deposit problem created by the introduction of tetraethyl lead, various lead scavengers have been added to the fuel. The introduction of these materials reduces the engine deposits which would accompany the combustion of the fuel containing tetraethyl lead alone, but their introduction is accompanied by a small but definite increase in wear rate. When oil-soluble lead naphthenates or sulfonates or lead salts of fatty acids are added to heavier stocks having sulfur contents

much higher than those which are encountered in leaded gasolines, marked decreases in engine wear are observed without any accompanying increase in engine deposits even though no scavenger for lead is employed.

The base fuels which are employed in the composition may be broadly described as petroleum distillates boiling in the range about 350–750° F., having a high sulfur content above about 0.5% by weight, and having an A. P. I. gravity above 20 and ordinarily above 25. The sulfur compounds are predominantly sulfides, disulfides and thiophenes; the more reactive sulfur compound such as mercaptans usually are removed from the fuel by a sweetening process. Distillates boiling in this range and having an even higher sulfur content, for example above 1.0% by weight, are especially suitable for use in the composition. Thoroughly acceptable fuels for use in engines in service requiring frequent speed and low changes, such as automotive diesel engines, may be prepared by employing more volatile distillates such as distillates boiling in the range about 350–625° F. and having sulfur content in excess of 0.5% by weight in the composition of the invention. The base fuel may suitably be a straight run distillate of a high sulfur crude such as a West Texas crude oil or a Santa Maria crude oil. Blends of straight run and cracked distillates having high sulfur contents may also be used as the base fuel in the composition.

A number of oil-soluble lead naphthenates, lead sulfonates, and lead salts of fatty acids have been incorporated in diesel fuels and tested to determine their effect on the rate of engine wear. It appears that all oil-soluble lead naphthenates, lead sulfonates and lead salts of fatty acids are effective in reducing engine wear, but it is preferred to employ compounds of high molecular weight such as lead salts of high molecular weight acids such as sulfonic acids having molecular weights above about 400 and of naphthenic acids having molecular weights above about 225.

The lead sulfonates which are employed in the composition of this invention are lead salts of sulfonic acids prepared by sulfonating such materials as white oils, lubricating oil fractions, higher boiling fractions of SO_2 extracts of gas oils, and high boiling synthetic alkyl aryl compounds such as those prepared by alkylating benzene with propylene polymers or with butylene polymers or with mixed propylene-butylene polymers. The sulfonic acids preferably have molecular weights above about 400 so that the resulting lead sulfonates have high solubilities in oil and relatively little solubility in water. The lead sulfonates may be prepared by heating litharge and the sulfonic acids while agitating the mixture. The sulfonates may also be prepared by contacting the sulfonate of an alkali metal or of an alkaline earth metal in solution in a paraffinic oil with aqueous lead nitrate and alcohol. For example, 1300 grams of calcium sulfonate prepared from a sulfonic acid having a molecular weight above 400 was dissolved in 2 liters of a paraffinic petroleum distillate boiling in the range 185–290° F. The calcium sulfonate sample contained about 50% of unsulfonated oil. The solution of sulfonate in the petroleum distillate was washed with 200 milliliters of 190 proof ethyl alcohol and 546 grams of lead nitrate dissolved in 700 cc. of water. The lead nitrate solution and the calcium sulfonate solution were agitated with steam for a period of about 10 minutes. The mixture was allowed to stand and an upper oily phase and a lower aqueous phase separated. The oily phase containing the dissolved sulfonates was subjected to three additional treatments with lead nitrate solution, the amounts and method of contact being the same as those just described. The oily phase separated from the final contact with lead nitrate was washed with ethyl alcohol and water. A small amount of lead oxide was added to the oily phase to neutralize any residual acidic material and the oily phase was permitted to stand on a steam plate overnight. The oily phase was then topped at 350° F. under 8 millimeters pressure to remove the paraffinic solvent. A lead sulfonate concentrate was recovered which was suitable for use in the fuel composition of this invention.

The lead naphthenates which are employed in the composition of this invention may be prepared in the following manner: A straight-run distillate from a naphthenic crude oil, for example a heavy gas oil having a molecular weight in the range 260–270, is washed with dilute caustic such as 3–8° Bé. caustic. An aqueous phase containing sodium naphthenate is separated when the washing is complete. This aqueous phase is treated with 98% sulfuric acid to separate an oily phase comprising naphthenic acids and an aqueous phase comprising sodium sulfate. The oily phase is separated and distilled under a vacuum to separate non-acidic materials from the naphthenic acids. The naphthenic acids are heated to a temperature in the range 250–300° F. and litharge is slowly stirred into the acid at this temperature. After the addition of litharge has been completed the mixture is held at temperature for approximately half an hour. The mixture is then cooled and a low boiling petroleum distillate such as Stoddard solvent is added to dissolve the lead naphthenates. The solution is then filtered and the filtrate comprising a solution of lead naphthenates is recovered as a product. The solvent is added in such amount that the lead content of the solution is in the range about 20–28% by weight. This solution is added to the diesel fuel to produce the composition of this invention.

The lead salts of fatty acids which may be employed in the composition are lead oleate, lead palmitate, lead stearate and the like or lead soaps produced from unrefined fats. The methods of producing these materials are well known.

Lead naphthenates, lead sulfonates or lead salts of fatty acids are added to the base fuel in amounts sufficient to give the compounded fuel a lead content in the range 0.005–0.07% by weight; however, it is preferred to employ an amount of lead naphthenate or lead sulfonate sufficient to give the compounded fuel a lead content in the range 0.02–0.06% by weight. If the amount of these materials added to the base fuel is below that necessary to make the lead content at least as high as 0.005% by weight, relatively little effect on the wear characteristics of the fuel is observed. When the amount of lead sulfonate or lead naphthenate added to the fuel is in excess of that required to give the compounded fuel a lead content of 0.07%, the excess lead produces relatively little incremental effect on the rate of engine wear irrespective of the sulfur content of the fuel, and in addition a tendency toward heavier engine deposits during operation is observed. The effectiveness of the lead sulfonates and the lead naphthenates to reduce engine wear incident to the combustion of diesel fuels, espe-

cially high sulfur diesel fuels, is illustrated by the following examples.

Example 1

Two parallel tests were run. In one test a diesel fuel was burned without the addition of a lead sulfonate or naphthenate and the wear rate incident to its combustion was measured. In a second parallel run the same diesel fuel was employed, but lead naphthenate was added to the fuel in amount sufficient to give the fuel a lead content of 1.8×10^{-5} pound atoms per gallon, which would correspond to 0.053% lead by weight in the fuel. Inspections on the diesel fuel employed in both tests are as follows:

Sulfur	per cent by weight	1.15
A. P. I. gravity		33.0
Viscosity at 100° F. SSU		35.8
ASTM D–158 distillation:		
Start	°F.	376
10%	°F.	442
59%	°F.	510
90%	°F.	590
End point	°F.	680
Cetane number		43

The tests were conducted in a single cylinder Caterpillar diesel engine. Operating conditions during the tests were:

Jacket temperature	°F.	175
Sump temperature	°F.	150
Exhaust temperature	°F.	800

The pistons were equipped with radioactive piston rings and wear rates were obtained by determining the radioactivity of the lubricating oil employed with a Geiger counter. This method of determining wear rates has been published appearing in the "S. A. E. Journal," June 1949, at page 52. The validity and reliability of this method of determining wear have been fully established by checking and coordinating the results obtained in this type of test with those obtained with the same fuels in conventional tests for determining engine wear which are characterized by long periods of engine operation such as 200–400 hours, and direct measurements of engine wear. The wear rate in the test in which diesel fuel containing lead naphthenate was burned was found to be 40% of the wear rate observed when the diesel fuel without lead naphthenate was burned.

Example 2

The base fuel described in Example 1 was employed in the runs of this example. In the first run the fuel alone was burned and the wear rate was determined by the method described in Example 1. In the second run the base fuel containing lead sulfonate in an amount sufficient to give the compounded fuel a lead content of 0.053% by weight was burned and the wear rate was determined. The lead sulfonate employed in this example was prepared by alkylating benzene with polypropylene, a heavy alkane fraction boiling in the range about 625–750° F. was separated, this fraction was sulfonated with concentrated sulfuric acid, and the resulting sulfonic acid was neutralized with sodium hydroxide. The sodium sulfonate was reacted with lead nitrate to separate lead sulfonate which was added to the base fuel. The wear rate of the fuel containing lead sulfonate was 44% of that of the base fuel without the additive.

Example 3

The runs of Example 2 were repeated, but the lead containing additive employed in this example was a basic lead sulfonate prepared by reacting the alkane sulfonic acid of Example 2 with a stoichiometric excess of litharge to produce a basic lead sulfonate. The wear rate of the fuel containing basic lead sulfonate in amount sufficient to give the compounded fuel a lead content of 0.053% was 42% of that of the base fuel without any additive.

Example 4

Two 240-hour tests under operating conditions typical of field service (rated load and 175° F. water jacket) in a Caterpillar D–4400 engine were conducted. In one test a West Coast straight run diesel fuel was burned, and in the second test the same West Coast straight run diesel fuel containing added lead naphthenate in amount sufficient to give the compounded fuel a lead content of 0.053% was burned. The diesel fuel had the following inspections:

Gravity A. P. I.		32.8
Viscosity SSU at 100° F.		34.5
Sulfur, weight per cent		1.00
Conradson carbon 10% bottoms, weight per cent		0.05
Color ASTM		1½
Flash, P. M., ° F.		168
Neutralization number		0.03
Cetane number		45.4
Distillation ASTM D–158:		
Start	°F.	360
10%	°F.	417
30%	°F.	454
50%	°F.	492
70%	°F.	532
90%	°F.	592
95%	°F.	630
End point	°F.	685

The lead naphthenate was prepared in the manner described in Example 1 and had the following properties:

Lead content, weight percent	24.0.
Non-volatile residue, weight percent	64.0.
Flash point, tag open cup ° F	110.
Appearance	Clear.
Color	Gardiner 8.

Comparative wear data for these two runs are presented in the following table:

	West Coast Straight Run	Diesel Fuel
Sulfur, percent	1.0	1.0
Lead by wt. as Lead Naphthenate, percent	0.00	0.053
Top Ring Wt. Loss, mg./hr.	2.9	1.18
Top Ring Wear, percent	100	40.5
Cyl. Liner Wear, in./1,000 hrs.	0.0069	0.0033
Cyl. Liner Wear, percent	[1] 100	47.8

[1] Base fuel assigned 100% wear rate.

The above data clearly indicate that the use of lead naphthenate in a 1% sulfur fuel substantially reduces engine wear.

At the conclusion of the above tests, the engine was examined for deposits and an inspection of piston skirt deposits, ring groove deposits, and ring and valve sticking indicated that the employment of lead naphthenate, in the amount above indicated, in the high-sulfur fuel had no adverse effect on engine deposits. Within the limit of reproducibility of inspections of this kind

it clearly appeared that the fuel containing lead naphthenate was at least equal to the base fuel in respect to engine cleanliness.

It is known that lead naphthenates, when used in lubricating oils without the addition of inhibitors, accelerate bearing corrosion with both copper-lead and cadmium-silver bearings. In order to determine whether the employment of lead naphthenate in a diesel fuel adversely affected copper-lead bearing corrosion, the fresh lubricating oil and lubricating oil which had been used in 240-hour tests in a Caterpillar D–4400 engine burning a 1% sulfur fuel with and without the addition of lead naphthenate were tested in the 300° F. accelerated copper-lead strip corrosion test. The results obtained are tabulated below:

	300° F. Strip Corrosion Test (Cu-Pb) mg. wt. loss		
Test Hours	24	48	72
Test Oils:			
1. Unused Heavy Duty Motor Oil	0.7	0.7	0.4
2. Oil 1—Used 240 hrs.—1% S Fuel	2.6	2.7	2.6
3. Oil 1—Used 240 hrs.—1% S Fuel containing 0.053% Lead by Wt. as Lead Naphthenate	1.9	2.3	2.0
4. Unused Heavy Duty Motor Oil +0.24% Lead by Wt. as Lead Naphthenate	260	297	487

These data indicate that lead naphthenate when added to the fuel and burned normally in the engine does not contribute to the corrosion of copper-lead bearings since the results obtained are similar and within the reproducibility of the test which is ∓3 milligrams. The corrosivity of the lead naphthenate in the lubricating oil is indicated by the high strip weight loss obtained in test No. 4 in the above table.

Example 5

A West Coast straight run diesel fuel having a sulfur content of 3.36% was burned in a diesel engine with and without the addition of lead naphthenate. In both tests the engine was operated at a jacket temperature of 175° F., a sump temperature of 150° F., and an exhaust temperature of 800° F. When the fuel was burned without the addition of lead naphthenate, the wear rate of 2.15 milligrams per hour was observed. When the fuel was burned with lead naphthenate added in amount sufficient to give the fuel a lead content of 1.8×10^{-5} pound atoms of lead per gallon, the wear rate was 1.45 milligrams per hour.

The appended drawing is a graphical representation of data obtained during numerous runs in which diesel fuels having sulfur contents ranging from 0.7% by weight to 2.0% by weight and containing lead naphthenate in varying amounts were burned. The graphs clearly show the effectiveness of lead naphthenate in reducing engine wear incident to the combustion of diesel fuels having high sulfur contents above about 0.5% by weight. It is clear from the graphs that the addition of lead naphthenate in amount sufficient to give the diesel fuel a lead content of at least 0.01% by weight produces a significant reduction in engine wear. It is clear from the graphs that the addition of lead naphthenate in amounts beyond that necessary to give the fuel a lead content of about 0.06% by weight results in relatively little incremental wear reduction. It will be observed that a diesel fuel having lead naphthenate present in amount to give the fuel a lead content of 0.1% by weight is just slightly better than a diesel fuel containing lead naphthenate in amount sufficient to give the fuel a lead content of 0.05% by weight in respect to engine wear rate. Since the addition of larger quantities of lead naphthenate to the fuel tends to increase engine deposits, it is preferred to use lead naphthenate in amount not exceeding that necessary to give the fuel a lead content of 0.06% by weight of lead; the addition of lead naphthenate in this amount gives substantially all of the wear reduction which it is possible to obtain by adding lead naphthenate to the fuel, and as indicated in Example 4 above the addition of lead naphthenate in this amount has no adverse effect on engine cleanliness.

We claim:

1. A high-sulfur diesel fuel of improved wear characteristics comprising a diesel fuel oil boiling within the range of about 350° F. to about 750° F. having an API gravity above about 20° and characterized by the presence of at least 0.5% by weight of sulfur contained therein in the form of stably bound naturally occurring sulfur compounds and between about 0.005 and 0.07 weight per cent of lead in the form of oil-soluble lead compounds selected from the group consisting of naphthenates, sulfonates, and high molecular weight salts of fatty acids having about 14 to about 18 carbon atoms per molecule.

2. The fuel as defined by claim 1, wherein said weight per cent sulfur is at least 1.0 weight per cent.

3. A high-sulfur diesel fuel of improved wear characteristics comprising a diesel fuel oil boiling within the range of about 350° F. to about 750° F. having an API gravity above about 20° and characterized by the presence of at least 0.5% by weight sulfur contained therein in the form of stably bound naturally occurring sulfur compounds and between about 0.005 and 0.07 weight per cent of lead in the form of an oil-soluble lead naphthenate having a molecular weight above about 225.

4. A high-sulfur diesel fuel of improved wear characteristics comprising a diesel fuel oil boiling within the range of about 350° F. to about 750° F. having an API gravity above about 20° and characterized by the presence of at least 0.5% by weight of sulfur contained therein in the form of stably bound naturally occurring sulfur compounds and between about 0.005 and 0.07 weight per cent of lead in the form of an oil-soluble lead sulfonate having a molecular weight above about 400.

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