United States Patent Office 2,930,681
Patented Mar. 29, 1960

2,930,681

FUELS FOR COMPRESSION-IGNITION ENGINES

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No Drawing. Application September 30, 1957
Serial No. 687,167

6 Claims. (Cl. 44—74)

This invention relates to improvements in hydrocarbon fuels, and, more particularly, to hydrocarbon fuels suitable for use in compression-ignition engines, such as diesel engines.

Various problems beset the operators of compression-ignition engines, such as diesel engines. Most vexatious problems are those of corrosion of engine parts and of internal engine deposits due to certain contaminants, for example, sulfur compounds which are commonly present in diesel fuels. Such problems are fraught with losses in operating efficiency and increased maintenance costs. Clogging of the fuel filters by gum-forming materials in the fuel is also highly undesirable, since clogged filters cause engine stalling and require frequent replacement and/or cleaning. Rusting of the various portions of the engine systems: the fuel tank, fuel supply lines, fuel injectors, etc. is another serious problem. It is caused by water almost invariably present in the fuel as produced and/or picked up by "breathing" of the atmospheric moisture by the fuel storage tanks, during transportation by sea in tanker compartments, previously ballasted with sea water.

Especially aggravating to the operators of these engines is the malfunctioning of their fuel injection systems. An efficient operation of a compression-ignition engine primarily depends on an unimpeded, regular supply of the fuel through the injection system into the combustion chamber and on the cleanliness of the injection nozzles. Injection nozzles, or injectors, are delicate mechanisms, even though designed to withstand continuous rugged service at high temperatures. Clogging of and deposits on the various parts of the injectors interferes with the spray pattern of the fuel resulting in incomplete combustion, excessive exhaust smoke, loss of power, irregularity of operation, excessive wear and stalling of the engine. Whether the deposits take place on the orifice (tip) of the injection nozzle, or the valve needle (plunger), or the valve seat, they interrupt the uniform admission or spraying of the required amount of fuel and, on undergoing carbonization at the high temperatures of use, cause erosion of the metal surfaces and eventual breakdown of the nozzle.

A large number of additives to compression-ignition engine fuels have been proposed in the past to resolve the problems indicated hereinabove. Certain materials have been suggested as additives for the reduction of engine wear resulting from the presence of sulfur compounds in the fuel. A number of materials have been likewise suggested as additives to the fuel for the purpose of reducing deposits occurring in the various portions of the compression-ignition engine.

However, it is known that, while, in general, a specific fuel additive may help to reduce or to eliminate a particular undesirable property of the fuel or to improve a certain phase of the engine operation, the application of such an additive is apt to bring about new operational problems and/or aggravate an already existing secondary problem. When two or more additives are employed

to cure distinct undesirable properties of the fuel and to improve the operation of an engine, more problems affecting the behavior of the fuel and the operation of the engine are apt to take place. In fact, in an ideal case, a combination of two or more additives at best is capable of exerting their desirable effects without interfering with each other and/or without creating new operational problems.

Oil-soluble polyoxyalkylene ethers of alkyl phenols containing at least 8 carbon atoms in the alkyl portion thereof and from 4 to 7 alkylene oxide units in the polyoxyalkylene portion of their molecules have been recently reported in the art as additives to hydrocarbon fuels for use in compression-ignition engines. When thus employed, they effectively prevent undesirable deposits in the injectors and clogging of fuel lines and filters. These oil-soluble ethers are added to a base hydrocarbon fuel boiling at least above about 325° F. in very small amounts of 1% by weight or less, based on the fuel. When the resulting compounded fuel is employed to operate a compression-ignition engine, exhaust smoke and fuel consumption are considerably reduced owing to a substantial reduction of injector deposits.

It has been also reported that the presence of these ether additives in the fuel minimizes rusting of ferrous surfaces in the injection system, in the engine proper, and in the fuel supply tank and lines. However, while a certain reduction of the rusting tendency is often noticed, this reduction does not necessarily occur for all fuels used in compression-ignition engines. In a great many instances, despite the presence of these non-ionic oil-soluble polyoxyalkylene ethers of alkyl phenols in the fuel, it is observed that injector nozzles and other parts of the injection system, such as valve seats, plungers, etc., corrode very rapidly, particularly when the engine is stopped and allowed to cool at frequent intervals, as is common in the fields of construction and transportation. In addition, corrosion is quick to appear upon cooling of the engine on the internal walls of the combusttion chamber (engine cylinder). Although the polyoxyalkylene ether additives assure a regular operation of the engine by preventing injector deposits, they generally fail to eliminate corrosion of the injectors and other ferrous components of the engine.

I have now found that the introduction into a base hydrocarbon fuel boiling at least above about 325° C. and suitable for use in compression-ignition engines, such as diesel engines, of a small quantity of an ammonium salt of a sulfonic acid having molecular weights in the range from about 400 to 600 and of another small quantity of a polyoxyalkylene ether of an alkyl phenol, such as described hereinbefore, results in a substantial reduction of the rusting tendency of the fuel, while the injector system remains free of undesirable deposits. The weight ratios of the sulfonate to the ether in the resulting fuel composition which provide this reduction range from about 1:160 to about 1:7. Preferably the ratios of the sulfonate to the ether are from 1:80 to 1:10. The two components, the ether and the sulfonate, instead of merely adding their improving effects—the ether with respect to the prevention of injector deposits and filter clogging, and the sulfonate with respect to the supression of the rusting tendency of the fuel—display a definite synergism in that the rusting tendency is suppressed to a considerably greater degree than it would have been if the sulfonate were employed as the only additive. This synergistic effect is obtained when the total amount of the ether and the sulfonate in the fuel is equal to at least 0.01% by weight of the fuel. Ordinarily, amounts from 0.01% to 0.2% are adequate to achieve the optimum result.

The ammonium sulfonate component of the improved

fuel of my invention may be any suitable ammonium salt of an alkyl aryl sulfonic acid having molecular weights in the range from about 400 to 600, prepared by any convenient method known in the art. Such a sulfonate is "ashless." In other words when burned incorporated in the fuel in the engine cylinder, it leaves substantially no deposits. Examples of these sulfonates are ammonium salts of various oil-soluble alkylnaphthalene sulfonic and alkyl benzene sulfonic acids of the aforementioned molecular weight range. As specific examples of suitable sulfonates there may be named: ammonium didodecyl naphthalene sulfonate, ammonium dinonyl naphthalene sulfonate, ammonium salts of higher polypropylene (C_{18} and upward) benzene sulfonic acids, ammonium salts of dialkyl benzene sulfonic acids (e.g., didodecyl benzene sulfonic acids), ammonium salts of sulfonic acid obtainable as by-products of white oil refining (so-called mahogany sulfonic acids), etc. The oil-soluble sulfonate may be used pure or dissolved in a hydrocarbon solvent, such as a lubricating oil, mineral seal oil, etc.

The non-ionic oil-soluble ether component may be any polyoxyalkylene ether of an alkyl phenol prepared by alkylating phenol with an olefin containing at least 8, and preferably 9 to 18, carbon atoms under conditions adapted to furnish a predominantly monoalkyl phenol reaction product having an average of 1.0 to 1.25 alkyl groups per phenol molecule. The olefins employed for the alkylation of phenol may be straight-chain olefins, such as those produced in the Fischer-Tropsch synthesis; branched-chain olefins, such as those formed in the polymerization of propylene and butylene; or mixtures of branched- and straight-chain olefins which are recovered from a heavy cracked naphtha by selective adsorption with silica gel. Alcohols or alkyl chlorides with carbon chains of suitable length may be also employed as the alkylating agents. Preferably, mixtures of C_9 to C_{15} branched-chain olefins produced by polymerizing propylene are thus employed. The resulting alkyl phenol product, which may contain from 15 to 20% by weight of dialkyl phenols, is condensed with 4 to 7, and preferably 5 to 6, molecules of an alkylene oxide, such as ethylene oxide, propylene oxide, butylene oxide, or a corresponding glycol. Ethylene oxide is usually preferred. Particularly suitable alkyl phenyl polyoxyalkylene ethers are monoalkyl phenyl polyoxyethylene ethers containing an average of 12 alkyl carbon atoms and 5 to 6 oxyethylene groups. As pointed out in the prior art, a very small amount of the ether, of the order of 1% by weight or less, is sufficient to prevent effectively the clogging of fuel lines and filters. Generally, amounts in the range from 0.01 to 0.2 weight percent, based on the fuel, are used for the purpose. The same amounts of the ether are employed together with the sulfonate to achieve the enhanced synergistic anti-rusting action in the fuels in accordance with the present invention.

The actual preparation of the improved fuel compositions of the invention raises no particular difficulties. The ether and the sulfonate components are added in the necessary proportions to the fuel, either separately or as a combination, and are thoroughly distributed therein. This may be achieved either immediately after the completion of the refining treatment of the hydrocarbon fuel, or during its storage, or just preceding the use of this fuel in a compression-ignition engine.

The base fuel which may be improved, in accordance with the invention, may be a straight-run or a cracked petroleum distillate; or it may be a fuel derived from shale; or one produced synthetically, for instance, by the Fischer-Tropsch process. It may also be a mixture of two or more of the afore-mentioned fuels. The base fuels thus improved boil in the range from about 325° to about 750° F.; in other words, they are suitable for use in engines of the diesel type, and the like.

The unexpectedly enhanced reduction of the rusting tendency obtainable, in accordance with the invention, is illustrated by the following data from one of a series of rusting tests. In these test series at premium grade, highly refined, diesel fuel boiling between 345° and 510° F. was employed as a representative compression-ignition fuel. The test represents a modification of the standard test employed for determining rust-preventing characteristics of steam turbine oils, adapted by the American Society for Testing of Materials under the designation of ASTM–D–665–54. Substantially the same testing equipment and the same conditions were employed in the modified test: steel specimens, or coupons, were exposed in the fuel to the action of synthetic sea water at a temperature of 140° F. The difference in the procedure consisted in conducting the tests for a period of 6 hours instead of 24 hours, and in employing a comparison rating scale from 1 to 7 to define the extent of rusting. On this scale rating 1 corresponds to a substantially complete freedom from rust, while rating 7 refers to heavy rusting of more than 99% of the coupon's surface. Rating 4 corresponds to about 40% of the coupon's surface being covered with a light coating of rust. Other ratings indicate intermediate degrees of rusting between 1 and 4 and 4 to 7. Ratings from 1 to 3 are considered as satisfying for conventional engine operations.

As a representative oil-soluble non-ionic polyoxyalkylene ether of alkyl phenol for the addition to the base fuel, the test employed the product of condensation of ethyleneoxide and a predominantly monoalkyl (polypropylene) phenol characterized by an average number of 12 alkyl carbon atoms. This ether, furthermore, contained from 5 to 6 oxyethylene units in its molecular structure. As a representative sulfonate additive for the tests, there was employed ammonium dinonyl naphthalene sulfonate, either as such or as a solution in mineral lubricating oil.

TABLE I

Rusting test ratings of metal coupons for different combinations of base fuel, ammonium sulfonate and oil-soluble non-ionic ether

Test Run No.	Oil-Soluble Non-Ionic Ether, p.p.m.	0	100	200	400	600	1,000
	Sulfonate, p.p.m.						
1	0	7	----------	6.5	7	6.5	6
2	[1] 6	6	6	6	6	------	------
3	[1] 1.2	6	6	6	5	------	------
4	[1] 2.5	5	----------	2.5	1.5	------	------
5	[1] 3.75	4	----------	1.5	1.5	------	------
6	5.0	>3.0 (aver.)	<3.0 (aver.)	--------	2.0	------	------
7	10.0	3.5	----------	1.5	------	------	------
8	15.0	2.0	[2] >1.0	[2] >1.0	------	------	------
9	20.0	[3] >1.0	----------	----------	------	------	------
10	30.0	[2] >1.0	[3] >1.0	1.0	------	------	------

[1] Sulfonate used as a solution in mineral lubricating oil.
[2] Rating slightly higher than 1.0 but less than 1.5.
P.p.m.=parts per million parts by weight of the base fuel.
Aver.=average of three runs.

It is noted from the data in the above table that addition of the oil-soluble non-ionic ether alone in amounts from 100 to 1000 p.p.m. parts of the base fuel effected no perceptible reduction of the rusting tendency. Sulfonate added alone in amounts from 15 p.p.m. upwards does reduce the corrosion tendency; in amounts from 5 to 15 p.p.m. its effectiveness is slight. However, unexpectedly the corrosion tendency is significantly enhanced when the addition of the sulfonate is accompanied by the addition of the non-ionic ether in accordance with the invention. The improvement is particularly evident when the sulfonate is employed in amounts from about 2.5 p.p.m. and upward ("p.p.m." means parts per million parts by weight of the base fuel) in conjunction with the non-ionic oil-soluble ether added in amounts from

100 to 400 p.p.m. Usually from 5 to 15 p.p.m. of the sulfonate in combination with the aforementioned amounts of the ether will provide the desired anti-rusting effect. The optimum of rust inhibition is achieved by the combination of from 5 to 10 p.p.m. of the sulfonate and from 100 to 400 p.p.m. of the ether in the base fuel.

The results of the table clearly show that a small amount, from 0.01 to 0.2% by weight of the combination of oil-soluble non-ionic ether and ammonium sulfonate in weight ratios from about 80:1 to 7:1, synergistically reduces the rusting tendency of compression-ignition engine fuels.

In addition to the three essential components of the improved fuel compositions of this invention, i.e., a base fuel boiling above 325° F., an ammonium alkyl aryl sulfonate and an oil-soluble polyoxyalkylene ether of alkyl phenol, these fuel compositions may further contain small amounts of other conventional additives, for instance, cetane number improvers, dyes, etc., provided that the presence of these materials does not interfere with the synergistic antirusting action of the ether and sulfonate combination. It may be also observed that the sulfonate component need not be employed in a pure state, but may be introduced into the fuel as a solution in a hydrocarbon oil or another appropriate solvent, provided this oil, or solvent, is inert and does not interfere with the improvement of the invention or create additional operational problems.

Thus the fuel compositions of the invention markedly reduce the rusting problem in compression-ignition engines. At the same time they reduce injector deposits and filter clogging, and assure more efficient operation with the minimum of exhaust smoke.

While many modifications of the invention may be made without departing from its spirit and scope, it should be understood that the invention is not limited to the specific illustrative embodiments thereof in the specification, except as defined in the following claims.

I claim:

1. A fuel composition for use in the compression-ignition engine, under the conditions tending to induce rusting of the engine at internal operating temperatures owing to the presence of water contamination in the fuel and to frequent interruptions of the engine operation, said fuel composition consisting essentially of a hydrocarbon base fuel boiling from about 325 to about 750° F. and as a rust-inhibiting additive combination, from 2.5 to 10 p.p.m. of an ammonium salt of an alkyl aryl sulfonic acid selected from the group consisting of alkyl benzene sulfonic and alkyl naphthalene sulfonic acids having a molecular weight in the range of from about 400 to 600, and 200 to 400 p.p.m. of an oil-soluble polyoxyalkylene ether of a predominantly monoalkyl phenol, said ether having from 9 to 18 alkyl carbon atoms in its alkyl portion and from 4 to 7 oxyalkylene units of 2 to 4 carbon atoms in its polyoxyalkylene portion.

2. The composition of claim 1 wherein the ammonium salt of alkyl aryl sulfonic acid is present in amounts from 5 to 10 p.p.m.

3. The composition of claim 1 containing an ammonium salt of alkyl naphthalene sulfonic acid.

4. The composition of claim 1 wherein the oil-soluble polyoxyalkylene ether of an alkyl phenol is a polyoxyethylene ether of a monoalkyl phenol, the alkyl group whereof contains an average of 12 carbon atoms, and the polyoxyethylene portion contains from 5 to 6 oxyethylene groups.

5. The composition of claim 4 wherein the ammonium salt of an alkyl aryl sulfonic acid is ammonium dinonyl naphthalene sulfonate.

6. An anti-rust additive blend for use in hydrocarbon fuels boiling from about 325 to about 750° F. to reduce rusting of the engine at internal operating temperatures owing to the presence of water contamination in the fuel and to frequent interruptions of the engine operation, consisting essentially of 2.5 to 10 parts of an ammonium salt of an alkyl aryl sulfonic acid selected from the group consisting of alkyl benzene sulfonic and alkyl naphthalene sulfonic acids having a molecular weight in the range of from about 400 to 600, and 200 to 400 parts of an oil-soluble polyoxyalkylene ether of a predominantly monoalkylphenol, said ether having from 9 to 18 alkyl carbon atoms in its alkyl portion and from 4 to 7 oxyalkylene units of 2 to 4 carbon atoms in its polyoxyalkylene portion.

References Cited in the file of this patent

UNITED STATES PATENTS

2,582,733	Zimmer et al.	Jan. 15, 1952
2,739,050	Wisherd	Mar. 20, 1956
2,786,745	Stayner et al.	Mar. 26, 1957