United States Patent Office 3,047,373 Patented July 31, 1962

3,047,373

FUEL OILS HAVING IMPROVED COMBUSTION CHARACTERISTICS

Robert J. McGuire, Monroeville, Pa., assignor to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

No Drawing. Filed Dec. 21, 1959, Ser. No. 860,672
6 Claims. (Cl. 44—66)

This invention relates to improving the combustion characteristics of hydrocarbon oil fuels that normally tend to form substantial amounts of soot and smoke during combustion.

The petroleum industry has encountered a serious problem in satisfying the demand for middle distillate and heavier fuel oils that can be burned in fuel burners, such as those of the atomizing type and of the rotary wall flame type, with little or no accompanying formation of smoke or soot. Oils that are normally burned in oil burners of the types indicated are those of No. 2 grade or heavier, although somewhat lighter oils can be used. Although some smoke and soot formation may accompany combustion of any hydrocarbon oil where less than optimum combustion conditions are used, the problem is serious in the case of oils having an API gravity of less than 34°, as substantial smoking and soot formation will occur during combustion of such oils even when favorable combustion conditions are employed. The poor combustion characteristics of such oils are considered attributable to the relatively high proportion of aromatic components contained therein. Fuel oils having an API gravity of less than 34° will normally contain in excess of about 20 percent aromatics, for example, 25, 40 or even 60 percent or more of aromatic components, whereas lighter fuel oils will normally contain a substantially lower proportion of aromatics, for example, 15 percent or less. In the case of distillate oils, a high aromatics content usually signifies a large proportion of cracked distillates, as the latter are relatively rich in aromatics. The proportion of catalytically cracked distillate fuel oils in commercially marketed fuel oils has increased in recent years notwithstanding the relatively inferior burning qualities of such oils, because the demand for fuel oils of comparable boiling range has exceeded the available supply of straight-run oils.

Not only do low-gravity distillate oils containing large proportions of cracked distillate, that is, oils rich in aromatics, form greater quantities of soot during combustion than straight-run, high-gravity distillate oils, or similar oils low in aromatics, but also such oils form soot of different quality. Soot formed from the latter oils is a loosely deposited, low-density material having a low coefficient of heat transfer, whereas soot from the former oils is resinous, much denser and has a higher coefficient of heat transfer.

While the problem of obtaining clean combustion is especially serious in the case of distillate fuels, where fuel quality is of major importance, a combustion problem also exists in the case of residual fuel oils. Residual fuels, similarly as middle distillate fuel oils, have an API gravity less than 34° (API gravity for typical No. 6 fuel oils varies in the range of about 5° to 15°), and they also frequently contain exceptionally large proportions, for example 60 percent or more, of aromatic components. Residual fuels can contain relatively low-boiling aromatic components as well as higher boiling materials, as they are frequently diluted or cut back with lower boiling cracked distillate oils in order to reduce the viscosity of the heavier oils.

Although the combustion of fuel oils having an API gravity of less than 34°, and consequently a relatively large proportion of aromatics, will tend to produce soot and smoke in atomizing type burners, that is, burners in which the fuel oil is burned in the form of a spray of liquid droplets after mixture with air, combustion of such oils in rotary wall-flame type burners constitutes an especially severe problem. In the latter instance the fuel oil is burned in vapor form after vaporization of the fuel by impingement thereof on a hot metal surface.

Excessive smoking and soot formation during combustion of fuel oils is objectionable not only from the standpoint of cleanliness and air pollution, but also in that smoke and soot lead to stack deposits which may reduce burner draft and/or cause the stack temperature to rise to a dangerous point.

The present invention relates to improved hydrocarbon fuel oil compositions that have smoke and soot forming tendencies during combustion, whereby they are rendered more suitable for use as fuels in domestic oil burners of various types such as heating furnaces of the atomizing or rotary wall-flame type, combustion gas turbine engines, and the like. We have found that such improved fuel compositions can be obtained by incorporating in the fuel oil of the type described a small amount in the range of about 0.01 to 0.1 percent by weight of the oil, of an ester of a fatty acid containing 12 to 18 carbon atoms per molecule and a polyoxyethylene glycol whose average molecular weight is about 380 to 630. A specific example of an especially effective material for the purposes of this invention is the monoester of ricinoleic acid and polyoxyethylene glycol that has an average molecular weight of about 400. However, mono- and diesters of other fatty acids and other polyoxyethylene glycols of the classes described herein can be used. For example, there can be used the stearates, ricinoleates, oleates, and laurates of the high molecular weight polyoxyethylene glycols disclosed herein, specific examples of which are the monostearate, monooleate, and diricinoleate of polyoxyethylene glycol having an average molecular weight of about 400.

The exact mechanism by which the high molecular weight polyoxyethylene glycol esters of the above-indicated class function to reduce smoke and soot forming tendencies of fuel oils has not been definitely determined, and accordingly, we do not intend for the present invention to be limited to any particular theory of operation. It has been theorized that the high molecular weight polyoxyethylene glycol esters whose use is included by this invention possess a peculiar combination or balance of surface-active properties such as to promote a reduction in the size of the fuel droplets sprayed into the combustion zone of the burner and/or an improvement in the spray pattern. This view is more or less supported by the fact that lower molecular weight polyoxyethylene glycol esters produce substantially inferior results with respect to smoke and soot formation during combustion of fuel oils, notwithstanding that these lower molecular weight materials contain the same functional groups and the same monomeric units. It also appears that the polyoxyethylene glycol esters disclosed herein also function in part in some way not connected with surface activity, as the materials disclosed herein reduce smoking of fuel oil burned from a wick, where no fuel spray is involved.

As indicated above, any fuel oil-soluble ester of a fatty acid having 12 to 18 carbon atoms per molecule and a polyoxyethylene glycol having an average molecular weight of about 380 to 630 can be used in the fuel oil compositions of this invention. The esters whose use is included by this invention can be prepared by well-known methods. For example, both the mono- and diesters can be prepared by simple esterification of the desired fatty acid and the desired polyoxyethylene glycol in a mole ratio such as to provide the desired product. Alternatively, the monoesters can be prepared by merely react-

ing an excess of ethylene oxide with the desired fatty acid. If desired, the diesters can also be prepared from the thus-obtained monoesters by further esterification with additional fatty acid.

It is of utmost importance for the purposes of the present invention that the polyoxyethylene glycol residues of the esters disclosed herein have an average molecular weight of at least about 380, as esters of lower molecular weight polyoxyethylene glycols are substantially inferior with respect to the property of reducing smoke and soot formation in fuel oils. Apparently, the esters of the lower molecular weight polyoxyethylene glycols do not possess the balance of surface-active properties that is necessary to reduce the fuel droplet size and improve the fuel spray pattern in the combustion zone. As also indicated, esters of fatty acids, especially monoesters of olefinically unsaturated 18 carbon atom fatty acids, and polyoxyethylene glycols having an average molecular weight of about 380 to 630 are especially effective for the purposes of the present invention. An example of a preferred polyoxyethylene glycol whose higher fatty acid esters are useful for the present invention is a polyoxyethylene glycol having an average molecular weight of about 400. A material of this kind having the desired molecular weight characteristics is marketed under the name Polyethylene Glycol 400.

Any higher fatty acid containing 12 to 18 carbon atoms per molecule that does not adversely affect the fuel oil solubility and the combustion improving characteristics of the polyoxyethylene glycol esters disclosed herein can be used to form said esters. Such fatty acids can be saturated and unsaturated or unsubstituted or substituted with non-hydrocarbon substituents such as hydroxyl, halogen, or the like. In fact unusually effective results appear to be obtainable when the acid component of the ester is substituted. For example, outstanding results have been obtained with esters of hydroxy-substituted mono-olefinic fatty acids, such as ricinoleic acid. Examples of other preferred fatty acids that can be used to form the esters disclosed herein are oleic acid, stearic acid, and linoleic acid. Examples of other fatty acids that can be used to form the esters disclosed herein are lauric acid, myristic acid, and palmitic acid.

The esters disclosed herein can be employed in fuel oils in any proportion that will reduce the smoke and soot forming tendencies of the oils. The optimum ester proportion in any given case can vary in accordance with the individual ester and in accordance with the nature of the fuel oil, as all of the esters disclosed herein are not exactly equivalent in their ability to improve the combustion characteristics of fuel oils, and as all fuel oils are not equally responsive to such esters. Normally some improvement in the combustion characteristics of fuel oils of the kind disclosed herein will be obtained by the use of as little as 0.01 percent of the esters disclosed herein. Best results are normally obtainable by the use of ester proportions in the range of about 0.03 to 0.07 percent by weight of the fuel oil. Normally, no additional advantage with respect to smoke and soot formation during combustion is obtained by the use of amounts in excess of about 0.1 percent by weight of the fuel oil. In fact, amounts in excess of 0.1 percent can be objectionable from the standpoint of haze formation in fuel oils, particularly in the case of the higher molecular weight polyoxyethylene glycol esters, because of the limited solubility in hydrocarbons of many of these materials.

The esters disclosed herein can be added to the fuel oils whose combustion characteristics are to be improved either as such, or in the form of concentrated solutions in solvents such as kerosene, or toluene. If desired, the esters disclosed herein may also have included therewith other addition agents designed to improve one or more properties of the fuel oil. Some agitation is usually desirable when mixing the herein disclosed esters with

fuel oil in order to facilitate rapid formation of a homogeneous mixture, but agitation is not essential.

As indicated the polyoxyethylene glycol esters disclosed herein are useful in conjunction with any fuel oil that normally tends to form substantial amount of smoke and soot during combustion. Such oils are normally of the middle distillate or heavier grades such as so-called No. 2, No. 4, No. 5, and No. 6 fuel oils, and the use of such oils is included by the present invention. Fuel oils of these grades are defined in the ASTM Standards on Petroleum Products and Lubricants under the ASTM Specification D–396. The invention is especially important in connection with fuel oils having an API gravity of less than 34°, particularly when these oils contain an excess of about 20 percent aromatic hydrocarbons, as such oils involve serious smoke and soot forming problems.

In order to demonstrate the effectiveness of the polyoxyethylene glycol esters disclosed herein, representative esters of the class disclosed were incorporated in separate samples of No. 2 fuel oils, and the thus-compounded fuel oils were subjected to two different combustion tests. In accordance with one of the test procedures employed, hereinafter referred to as the Smoke Lamp Test, the fuel to be tested was burned in a standard Institute of Petroleum Lamp. In carrying out the test the height of the lamp flame was adjusted until the smoke point was reached. At this flame height the combustion products of the fuel were drawn through a one-inch diameter No. 4 Whatman filter paper under a constant pressure differential of two inches of dibutylphthalate for two minutes, and the deposits on the filter paper were rated by means of a photo-cell meter that had been calibrated by a Bacharach-Shell smoke spot chart graduated in increasing shades of black ranging from 0 (clean disc) to 9 (black disc) as the standard.

The fuel oils employed in this test comprised different samples of the same fuel oil blend (tested at different times) hereinafter referred to respectively as Base Fuel A and Base Fuel B, of 35 percent West Texas straight run No. 2 fuel oil distillate and 65 percent catalytically cracked No. 2 fuel oil distillate having an API gravity of 30.9° and an aromatics content of 41.0 percent by weight.

Esters subjected to the smoke lamp test included the monoricinoleate of a polyoxyethylene glycol having an average molecular weight of about 400 and the monostearate of polyoxyethylene glycol. The monostearate employed in the smoke lamp test was a commercial product marketed under the name MYRJ–45. This material was a cream-colored semisolid having a specific gravity in the range of about 1.00 to 1.05. This material was substantially identical on the basis of a comparison of appearance, specific gravity, and solubility characteristics with a monostearate of a polyoxyethylene glycol having an average molecular weight of about 400.

The results of the above-described smoke lamp tests are set forth in the following table:

Table A

Test Fuel	Additive Concentration, Wt. Percent	Smoke Disc No.	Percent Reduction in Smoke Disc. No.
Base Fuel A		4.60	
+ Monoricinoleate of Polyoxyethylene Glycol	0.06	4.07	11.5
Base Fuel B		5.88	
+ Monosterarate of Polyoxyethylene Glycol	0.10	4.81	18

The test results set forth in the foregoing table clearly demonstrate the improvement in combustion characteristics obtainable by the polyoxyethylene glycol esters of the kind disclosed herein.

Fuel oils containing polyoxyethylene glycol esters of the class disclosed herein were also subjected to a full-

scale one-day smoke test in a domestic oil burner (Timken Model OFH–60 Hi-Furnace). Conventional burner controls were associated with the test apparatus in conjunction with electrical timer relays to provide 20-minute "on" and 10-minute "off" cycles of burner operation. After permitting a warm-up of at least one 20-minute "on" cycle of burner operation with maximum combustion air, smoke spot and CO_2 readings were taken at the middle of each "on" cycle for several cycles using different air gauge settings to regulate the quantity of combustion air. Changes of gate setting were made during burner "off" phases of the cycle. Smoke spot readings were obtained by withdrawing flue gas from a sampling probe installed in the chimney pipe through a disc of a No. 4 Whatman filter paper one inch in diameter for two minutes. A vacuum pump was used to maintain a pressure differential of 2¼ inches Hg across the disc. The smoke spot reading was determined as described above in connection with the smoke lamp test description. CO_2 readings were obtained by withdrawing flue gas through a sampling probe installed in a chimney pipe in accordance with United States Department of Commerce Bulletin CA104–46 and by analyzing the thus-withdrawn flue gas for percent CO_2 in an Orsat-type flue gas analyzer. The fuel oil employed in the above-described test, hereinafter referred to as Base Fuel C, was a blend of 35 percent by volume West Texas straight run and 65 percent by volume fluid catalytically cracked No. 2 fuel oil distillates having an API gravity of 29.3° and an aromatics content of 45.0% by weight.

The esters employed in the one-day smoke test comprised a commercial mixture of di- and tri-ricinoleates of a polyoxyethylene glycol having an average molecular weight of about 400 marketed under the name Polyethylene Glycol 400 (di-, tri-)ricinoleate, and the monoricinoleate of a polyethylene glycol having an average molecular weight of about 400 marketed under the name Polyethylene Glycol 400 (mono)-ricinoleate.

The results obtained in the one-day smoke test are set forth in the following table:

Table B

Test Fuel	Additive Proportion, Percent by Wt.	Avg. Smoke Spot No. 11 to 13% CO_2	Percent Reduction Smoke Spot No.
Base Fuel C		1.78	
Mixed Di- and Tri-Ricinoleates of Polyoxyethylene Glycol	0.06	1.71	3.9
+ Monoricinoleate of Polyoxyethylene Glycol	0.06	1.36	23.5

The results set forth in the preceding table demonstrate that polyoxyethylene glycol esters of the class disclosed herein are effective to reduce smoke and soot formation in actual operation in a domestic fuel oil burner. The results presented in the table also demonstrate singular effectiveness for monoesters of substituted olefinic fatty acids and polyoxyethylene glycols having a molecular weight in the preferred range.

It will be understood that the specific embodiments set forth hereinabove are illustrative only and that the invention is not limited to the use of such specific polyoxyethylene glycol esters.

Specific examples of other compounded fuel oils containing polyoxyethylene glycol esters of the type whose use is included by the present invention are indicated in the following table:

Table C

Addition Agent	Addition Agent Concentration, percent by Wt.	Base Fuel
Monolaurate of Polyoxyethylene Glycol, Avg. M.W. 400	0.06	Base Fuel A.
Monooleate of Polyoxyethylene Glycol, Avg. M. W. 600	0.06	Do.
Monoricinoleate of Polyoxyethylene Glycol, Avg. M.W. 600	0.06	Do.

If desired the fuel oil compositions of this invention may contain in addition to the compounds previously discussed oxidation inhibitors, corrosion inhibitors, antifoam agents, other ignition quality improvement agents, sludge inhibitors, color stabilizers, and/or other addition agents adapted to improve the oils in one or more respects.

Obviously, other modifications and variations of the invention as herein described may be resorted to without departing from the spirit or scope thereof. Therefore, only such limitations will be imposed as are indicated in the appended claims.

I claim:

1. A fuel oil composition comprising a major amount of a hydrocarbon fuel oil that has an API gravity less than 34° and an aromatics content greater than 20 percent and that normally tends to form smoke and soot during combustion, and containing an amount sufficient to reduce the smoke and soot forming tendencies of the oil in the range of about 0.01 to 0.1 percent by weight of the oil of an ester of a fatty acid containing 12 to 18 carbon atoms per molecule and a polyoxyethylene glycol whose average molecular weight is about 380 to 630.

2. The fuel oil composition of claim 1 where said fuel oil is a distillate fuel oil.

3. The fuel oil composition of claim 1 where the amount of said ester is in the range of about 0.03 to 0.07 percent by weight of the oil.

4. The fuel oil composition of claim 1 where said fatty acid is an olefinic fatty acid.

5. The fuel oil composition of claim 1 where said ester is the monoricinoleate of a polyoxyethylene glycol having an average molecular weight of about 400.

6. The fuel oil composition of claim 1 where said ester is the monostearate of a polyoxyethylene glycol having an average molecular weight of about 400.

References Cited in the file of this patent

UNITED STATES PATENTS

557,291	Tempere	Mar. 31, 1896
1,331,054	Dinsmore	Feb. 17, 1920
2,548,347	Caron et al.	Apr. 10, 1951

FOREIGN PATENTS

701,459	Great Britain	Dec. 23, 1953
711,364	Great Britain	June 30, 1954

OTHER REFERENCES

"Polyethylene Glycol Esters," by Kessler Chemical Co. Inc., Philadelphia, 1948, pages 3–10.