

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Hydrocarbon Distillate Fuel Compositions

We, ETHYL CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, of 100, Park Avenue, New York 17, State of New York, 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:—

The present invention relates to improved liquid hydrocarbon distillate heating or lighting fuels, such as kerosene or fuel oil but does not apply to gasoline.

According to the invention, we provide a liquid hydrocarbon distillate heating or lighting fuel such as kerosene or fuel oil but excluding gasoline containing from 0.01 to 5 weight percent of manganese as a cyclopentadienyl manganese tricarbonyl compound.

Our improved distillate hydrocarbon fuels are capable of higher burning rates with improved efficiency and less soot formation.

The manufacture of the cyclopentadienyl manganese tricarbonyl compound as well as its use in fuel (e.g. gasoline) is described in greater detail in prior Patent Specification No. 781,065.

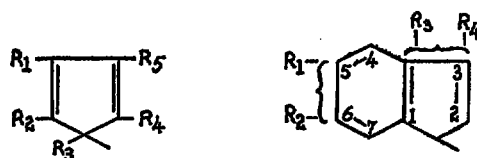
The cyclopentadienyl radical preferably contains 5 to 13 carbon atoms. As will be seen below, such compositions give rise to a great reduction in soot formation with an increase in burning efficiency.

For most applications beneficial results are realized when from 0.05 to 2.0 weight percent manganese is present in the fuel as a cyclopentadienyl manganese tricarbonyl compound.

There are three primary constituents in our additive compounds. They are the metallic constituent manganese, the cyclopentadienyl radical and an electron donating group, namely, the carbonyl radical.

The cyclopentadienyl radical can be represented by the formulae

[Price 4s. 6d.]



where the R's are hydrogen or univalent organic hydrocarbon radicals.

A preferred class of radicals suitable in the practice of this invention are those which contain from 5 to about 13 carbon atoms. These are exemplified by cyclopentadienyl, indenyl, methylcyclopentadienyl, propylcyclopentadienyl, diethylcyclopentadienyl, phenylcyclopentadienyl, *tert*-butyl-cyclopentadienyl, *p*-ethyl-phenylcyclopentadienyl and 4-*tert*-butyl indenyl. The compounds from which these are derived are preferred as they are the more readily available cyclopentadienyl compounds and the metallic cyclopentadienyl coordination compounds obtainable from them have the more desirable characteristics of volatility and solubility which are prerequisites of superior hydrocarbon additives. Moreover, they give the most outstanding results.

Thus, representative compounds of the present invention include cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, methyl indenyl manganese tricarbonyl, fluorenyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, methylpropylcyclopentadienyl manganese tricarbonyl and phenylcyclopentadienyl manganese tricarbonyl.

The preferred compounds are liquids at ordinary temperatures so that they can be readily handled and easily blended with liquid hydrocarbons. An outstanding example of this class of compound is methylcyclopentadienyl manganese tricarbonyl.

The additives of this invention may be conveniently prepared by reaction of the corresponding bis(cyclopentadienyl) manganese compound with carbon monoxide under pressure.

5 The identity of the cyclopentadienyl radicals in this intermediate corresponds to those desired in the final product. The bis(cyclopentadienyl)manganese intermediates can, in turn, be conveniently prepared by reaction of
10 a cyclopentadienyl alkali metal compound such as cyclopentadienyl sodium with a manganese salt such as manganous chloride.

The base fuels employed are generally liquid hydrocarbons; derived by distillation from crude petroleum and include those distillation fractions suitable for use in various burning functions which produce light and/or heat in a system other than a spark ignition internal combustion engine. Thus the fuels generally
15 have initial evaporation temperatures of above about 105°F. and final boiling points of from about 375°F. to about 700°F. The common names applied to the liquid hydrocarbon fuels employed include lamp oil, heating oil, kerosene, light petroleum distillate, stove oil, gas oil, household heating fuels, light industrial fuels, heavy industrial oils, stove and lamp
20 naphtha, Number 2 heater fuel or furnace oil and diesel fuels (which may alternatively be employed in heating functions.) These fuels differ from gasoline not only in the use to which they are put but in their physical properties. Gasoline, for example, is a specific cut or blend of petroleum hydrocarbons which
25 has a maximum initial boiling point up to about 105°F. and a final boiling point never in excess of about 440°F. In addition, gasoline ordinarily has a flash point below 32°F. whereas the fuels employed in the compositions of this invention ordinarily will not flash below
30 about 100°F. Furthermore, the great majority of fuel compositions employed by us have initial boiling points in excess of 150°F.

In order to test the efficiency of burning of a petroleum distillate fuel an apparatus similar to a kerosene wick lamp is often employed. Several methods of determining burning efficiency are available with such an apparatus and include the measurement of the
35 flame height at the point of incipient soot formation. Alternatively the apparatus may be operated at the incipient soot point and the soot formed collected for a definite period of time. Comparison of either the flame height at incipient soot point or the deposit weight per unit time at incipient soot point of a fuel containing an additive with the corresponding
40 results obtained in the same fuel without additive is an excellent measure of the increase or decrease in burning efficiency which is imparted by the additive. Another approach is to operate the apparatus at the incipient soot point and measure the specific fuel consumption. It is obvious that an increase in specific
45 fuel consumption at the incipient soot point is

an indication of the efficiency with which a fuel may be burned under controlled conditions of air supply.

When the latter procedure was employed using a fuel composed of 70 percent kerosene, 20 percent light naphtha in the boiling range of 300 to 400°F. and 10 percent distillate hydrocarbons having an end point higher than kerosene, with no additive, the specific burning rate in the apparatus employed at an air flow rate of 5 liters per minute was found to be 2.68 grams of fuel per hour. When this same fuel under identical conditions contained in addition approximately 0.058 weight percent manganese as cyclopentadienyl manganese tricarbonyl the burning rate was increased to 2.98 grams of fuel per hour. This represents better than an 11 percent increase in the specific fuel consumption and therefore an outstanding increase in fuel combustion efficiency is achieved. Similarly when as little as 0.014 weight percent manganese as cyclopentadienyl manganese tricarbonyl was added to the fuel a significant increase in fuel consumption rate was attained.

The following examples, in which all parts and percentages are by weight, illustrate various specific embodiments of the compositions of this invention employing liquid hydrocarbon distillate fuels.

EXAMPLE I

To a typical petroleum derived kerosene (1000 parts) having an initial evaporation temperature of 325°F. and a final evaporation temperature of 565°F. is added with agitation 17.9 parts of cyclopentadienyl manganese tricarbonyl. The agitation is continued until a homogeneous blend containing 0.5 weight percent of manganese is achieved. The resulting fuel composition when employed in kerosene lamps or jet burners is found to have superior combustion characteristics than the fuel which contains no cyclopentadienyl manganese tricarbonyl.

EXAMPLE II

To 10,000 parts of a hydrocarbon fuel designated as No. 1 heater oil which has an initial evaporation temperature above 350°F. is added methylcyclopentadienyl manganese tricarbonyl in amount sufficient to give a composition of about 5 percent manganese by weight.

EXAMPLE III

To 1000 parts of fuel suitable for use in jet burners having a 10 percent evaporation point of 220°F., a 90 percent evaporation temperature of 470°F., an end point of 550°F. and an API gravity of 45° is added a sufficient quantity of octyl cyclopentadienyl manganese tricarbonyl to give a fuel composition containing 2 percent by weight of manganese. This fuel is found to have improved combustion characteristics over the corresponding fuel without the octyl cyclopentadienyl manganese tricarbonyl in that it burns with a cleaner



illustrate specific

flame at a higher fuel consumption rate and leaves a minimum of deposits on the interior surface of the apparatus in which it is used.

EXAMPLE IV

To 1000 parts of a furnace oil designated No. 2 heater oil which has an initial evaporation temperature in excess of 380°F. is added with agitation sufficient indenyl manganese tricarbonyl to give a composition containing 0.01 weight percent manganese.

EXAMPLE V

An improved kerosene blend according to this invention is prepared by adding to 1000 parts of a kerosene having a 10 percent evaporation point of 380°F. and a 90 percent evaporation point of 480°F., sufficient ethylcyclopentadienyl manganese tricarbonyl to give a composition containing 1 weight percent manganese.

EXAMPLE VI

To 10,000 parts of a standard heater oil designated as No. 1 distillate fuel having an evaporation range of from 330 to 565°F. is added sufficient phenylcyclopentadienyl manganese tricarbonyl to give a composition containing 0.5 weight percent manganese. This fuel is employed as a domestic heater fuel to give cleaner more efficient burning than the fuel which does not contain the phenylcyclopentadienyl manganese tricarbonyl.

EXAMPLE VII

To a fuel suitable for use in jet burners having a 10 percent evaporation point of 160°F. and an end point of 600°F. is added methylcyclopentadienyl manganese tricarbonyl in amount sufficient to produce a final composition containing 0.07 percent manganese which is eminently suited for use as a fuel in jet engines.

EXAMPLE VIII

Ethyl methylcyclopentadienyl manganese tricarbonyl, in amount sufficient to give a composition containing 1.5 weight percent manganese is added to a fuel suitable for use as a heater or diesel fuel. This fuel has an initial evaporation temperature of 350°F. and an end point of 580°F. When employed either in heating or diesel applications it is found to

be a cleaner burning fuel than the base fuel without ethyl methylcyclopentadienyl manganese tricarbonyl.

In many applications petroleum distillate fuels are employed in conjunction with other additives beside the cyclopentadienyl manganese tricarbonyl compounds as employed in this invention for improving the burning efficiency of the fuel. These other additives usually comprise antioxidants, dyes, stabilizers, dispersants, corrosion inhibitors, cetane improvers and sludge inhibitors. It is therefore within the perview of this invention to employ liquid hydrocarbon distillate fuels containing a cyclopentadienyl manganese tricarbonyl compound in conjunction with such additives. Typical of the antioxidant materials employed are alkylated phenols such as 2,6-di-*tert*-butyl phenol, 4,4'-methylene bis-2,6-di-*tert*-butyl phenol, 4-amino-2,6-di-*tert*-butyl phenol, and 2,6-di-*tert*-butyl-4-methyl phenol and amines such as N,N'-di-*sec*-butyl-*p*-phenylenediamine and *p*-*n*-butylaminophenol. A typical sludge inhibitor is a copolymer of lauryl methacrylate and diethylamino ethylmethacrylate, while various amines and sulfonates are often employed as dispersants. In addition various phosphorus and boron compounds are frequently employed to impart improved stability to the fuels.

WHAT WE CLAIM IS:—

1. A liquid hydrocarbon distillate heating or lighting fuel such as kerosene or fuel oil but excluding gasoline containing from 0.01 to 5 weight percent of manganese as a cyclopentadienyl manganese tricarbonyl compound.
2. A fuel according to claim 1 containing from 0.05 to 2 weight percent of manganese as a cyclopentadienyl manganese tricarbonyl compound wherein the cyclopentadienyl group contains from 5 to 13 carbon atoms.
3. A liquid hydrocarbon heating or lighting fuel substantially as herein described and as set forth in the foregoing Examples.

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