Patented Feb. 6, 1945 2,368,866

UNITED STATES PATENT OFFICE

2,368,866

TRIALKYL PHOSPHINES FOR DIESEL FUELS

Edwin M. Nygaard and John H. McCracken, Woodbury, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

No Drawing. Application October 22, 1941, Serial No. 416,048

3 Claims. (Cl. 44—57)

This invention relates to fuels for internal combustion engines of the Diesel or compression ignition type, and more particularly relates to the improvement of such non-viscous hydrocarbon fuels by the addition thereto of a characterizing agent.

In Diesel engine operation, a liquid fuel is injected into a combustion chamber and ignited by compression. In order to obtain maximum efficiency, the delay period between the instant of injection and the instant of ignition should be short. Improperly delayed ignition gives rise to the phenomena known as "knocking" due to improper coordination of combustion and cylinder characteristics. By accelerating the ignition point of Diesel fuel it is possible to lower the compression pressure, which will insure spontaneous ignition without combustion shock, thereby increasing the ease of starting and smoothness with which combustion takes place.

As is well known to those more familiar with the art, various compounds have been credited with the capacity to improve the ignition quality of Diesel fuels. Small amounts of such compounds incorporated in the fuel act as ignition accelerators. By such means, the better grades of Diesel fuels are improved, and the low grade fuels are improved so as to have greater value.

The present invention is predicated on the discovery that the ignition delay period of non-viscous hydrocarbon fuel oils used in Diesel type engines, is decreased substantially by the addition thereto of a trialkyl phosphine. The trialkyl phosphines are compounds characterized by the general formula



wherein, R_1, R_2, and R_3 represent alkyl radicals and the radicals represented by R_1, R_2, and R_3 may be the same or different alkyl groups. Typical alkyl radicals which may be present in the alkyl phosphines contemplated herein are methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, ter-butyl, etc.

This invention contemplates Diesel fuels containing tri-alkyl phosphines of the foregoing types. Contemplated also by this invention is an improved method of accelerating the ignition of a non-viscous hydrocarbon fuel oil in compression ignition engines, said method being characterized by the step of admixing a trialkyl phosphine with the fuel prior to its ignition in the engine.

Various methods of preparation of trialkyl phosphines are known to those skilled in the art. Reference to the literature provides the following list of typical methods:

A. Berle, Jahresber. Fortschr. Chem. 1855, 590. Sodium-phosphorous alloy is treated with ethyl iodide.

B. A. Cahours and A. W. Hofmann, Ann. 104, 1, (1857). The reaction of phosphorous trichloride with a solution of diethyl zinc in ether gives the zinc chloride salt of triethyl phosphine. The free phosphine is obtained by distillation from alkaline solution.

C. A. W. Hofmann, Ann. Supl. 1, 4 (1861–2). A. Cahours, Ann. 122, 329 (1862). Phosphorous-zinc alloy, or a mixture of phosphorous and zinc is treated at elevated temperature and pressure with ethyl iodide.

D. Drechsel and Finkelstein, Ber. 4, 352 (1871). Zinc hydrogen phosphide, from diethyl zinc and phosphine, is treated with ethyl iodide to give the hydriodide of triethyl phosphine.

E. A. W. Hofmann, Ber. 4, 205, 372 (1871). Phosphonium iodide treated with ethanol at 180° C. gives the hydriodide of triethyl phosphine.

F. Hibbert, Ber. 39, 160 (1906). Ethyl magnesium bromide treated with phosphorous tribromide followed by dry distillation gives triethyl phosphine.

G. W. C. Davies, et al. J. Chem. Soc. 1929, 33, 1262; 1930, 2298; 1931, 575; 1932, 2880; 1933, 1043; 1935, 462. The method is essentially that of the preceding reference, the main exception being the method of decomposing the Grignard reaction mixture and recovery of the product.

As examples of the trialkyl phosphines, we have prepared triethyl phosphine by the method proposed by Hibbert (reference F), and tributyl phosphine by the method proposed by Davies et al. (reference G) and these procedures, which are typical methods for preparing compounds of the general class contemplated herein, are described in the following illustrative examples:

Example I

Triethyl phosphine

In a three-necked flask of suitable size, fitted with a stirrer, reflux condenser and dropping funnel, were placed 35.4 parts of anhydrous ethyl ether and 4.86 parts of magnesium turnings. To the magnesium and ether were gradually added 21.8 parts of ethyl bromide. To the cooled Grignard solution were gradually added 6.0 parts of phosphorous tribromide (prepared by the method in Organic Syntheses, vol. XIII, pg. 21) dissolved in 2.49 parts of anhydrous ether. The reaction mixture was transferred to a distilling flask and the ether was distilled. The distilling flask was then surrounded with an oil bath and the triethyl phosphine driven out by gradually raising the oil bath temperature to 195° C. Care was taken to prevent exposure of the product to

the air. This distillate was found to be 43 per cent. triethyl phosphine.

EXAMPLE II

Tributyl phosphine

In a three-necked flask of suitable size, fitted with stirrer, reflux condenser and dropping funnel were placed 14.2 parts of anhydrous ethyl ether and 2.5 parts of magnesium turnings. 13.7 parts of butyl bromide were added gradually. To the cooled Grignard solution were slowly added 6.8 parts of phosphorous tribromide (prepared as in Example I above) dissolved in 4.0 part of anhydrous ether. The reaction mixture was refluxed for thirty minutes and then cooled to 0° C. A solution of 13.0 parts of ammonium chloride in 65 parts of water was carefully added. After stirring for one hour, most of the magnesium hydroxide had redissolved. The ether layer was separated from the aqueous portion, which was extracted twice with small portions of ether. The extracts were combined and dried over anhydrous sodium sulfate. The ether was removed by distillation and the portion of the residue boiling at 95° C.–105° C. at 8 m. m. collected as the product. The yield was 54 per cent. of the theoretical.

The effectiveness of the trialkyl phosphines in improving the ignition qualities of Diesel fuels is demonstrated by comparative results of a fuel blank and a fuel blend. The fuel used was a catalytically cracked No. 2 fuel oil, which has an A. P. I. gravity of 28.8, flash point of 200° F., aniline point of 122° F., and a cetane number of 33.0. The ignition quality of the fuel and the fuel blend was determined by comparison with a standard reference fuel in a converted C. F. R. engine using the ignition delay method. The value obtained in this test is expressed as the "cetane number" which is the per cent. by volume of cetane and alphamethyl naphthalene having the same combustion characteristics as the sample under test (Reference: Proc. Am. Soc. Testing Materials, vol. 36, I, 418 (1936)).

Typical trialkyl phosphines, triethyl phosphine, and tributyl phosphine, prepared as described above, are illustrative of the class of compounds contemplated here as ignition accelerators. The effectiveness of such compounds in the aforesaid non-viscous hydrocarbon fuel oil is shown in Table I given below:

TABLE I

Compound added	Per cent (by wt.) added	Cetane No. of blend	Increase in cetane No.
Triethyl phosphine	0.45	37.5	4.5
Tributyl phosphine	1.0	36.0	3.0
Do	0.5	34.0	1.0

It appears that the triaryl phosphines are not effective, as a class, to improve the ignition quality of representative non-viscous hydrocarbon fuel oils. For example, a saturated solution, containing less than 2 per cent. of triphenyl phosphine in a typical Diesel fuel actually decreased the cetane number of the fuel. Our invention, therefore, is restricted to the trialkyl phosphines.

For the purpose of this invention, the trialkyl phosphines contemplated herein may be used in amounts of from about 0.1 per cent. to about 5.0 per cent., and preferably from about 0.25 per cent. to about 2.0 per cent.

It is to be understood that the foregoing examples are illustrative only and not to be interpreted as in any way limiting this invention. Similarly, it is to be understood that the terms "Diesel fuel," "Diesel type fuel," "hydrocarbon fuel oil," etc., as used herein are inclusive of all types of non-viscous hydrocarbon fuel oils intended for use in any compression ignition engine.

We claim:

1. The method of operating an internal-combustion engine of the compression ignition type wherein a fuel is injected into compressed air in the engine cylinder and ignites spontaneously therein, which comprises injecting into the compressed air in the engine cylinder a liquid hydrocarbon fuel which would normally cause knocking due to delayed ignition, and admixing with the fuel prior to such injection from about 0.1 per cent to about 5.0 per cent., to shorten the ignition delay period of said fuel, of a compound represented by the general formula



wherein R_1, R_2 and R_3 represent alkyl radicals.

2. The method of operating an internal-combustion engine of the compression ignition type wherein a fuel is injected into compressed air in the engine cylinder and ignites spontaneously therein, which comprises injecting into the compressed air in the engine cylinder a liquid hydrocarbon fuel which would normally cause knocking due to delayed ignition, and admixing with the fuel prior to such injection from about 0.1 per cent., to shorten the ignition delay period of said fuel, to about 5.0 per cent. of triethyl phosphine.

3. The method of operating an internal-combustion engine of the compression ignition type wherein a fuel is injected into compressed air in the engine cylinder and ignites spontaneously therein, which comprises injecting into the compressed air in the engine cylinder a liquid hydrocarbon fuel which would normally cause knocking due to delayed ignition, and admixing with the fuel prior to such injection from about 0.1 per cent., to shorten the ignition delay period of said fuel, to about 5.0 per cent. of tributyl phosphine.

EDWIN M. NYGAARD.
JOHN H. McCRACKEN.