Patented Dec. 7, 1943

2,335,953

# UNITED STATES PATENT OFFICE

2,335,953

## DIESEL FUEL

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No Drawing. Application May 2, 1942
Serial No. 441,536

7 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.

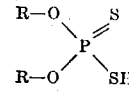
In Diesel engine operation, a liquid fuel is injected into a combustion chamber and ignited by compression. In order that maximum efficiency be attained, the delay period between the instant of injection and the instant of ignition should be short. Improperly delayed ignition, or improper coordination of combustion and cylinder characteristics, gives rise to the phenomenon known in the art as "knocking." By accelerating the ignition of the 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 and consequent operation of the engine takes place.

As is well known to those familiar with the art, numerous compounds have been proposed for use in Diesel fuels to improve the ignition quality of said 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 upon the discovery that Diesel fuels of improved ignition quality can be obtained by admixing with the fuel a minor proportion of a reaction product of perchloromethylmercaptan ($Cl_3CSCl$) and a disubstituted dithiophosphoric acid.

Perchloromethylmercaptan, as indicated by the formula above, is a chlorine substituted sulfur chloride and can be prepared by the chlorination of carbon disulfide according to the method of Helfrich and Reid (J. Amer. Chem. Soc. 43, 591 (1921)). For example carbon disulfide containing about 0.4% by weight of iodine was chlorinated in the absence of direct sunlight at a temperature maintained below 25° C. until the volume of the reaction mixture had doubled. The crude product, which has been topped to remove carbon tetrachloride and sulfur dichloride contains perchloromethylmercaptan, with some sulfur monochloride. This crude product can be used in the preparation of the reaction products contemplated herein, although in the examples cited herein a fractionated product was used.

In order to obtain our new and novel reaction products, perchloromethylmercaptan is reacted with a disubstituted dithiophosphoric acid represented by the formula

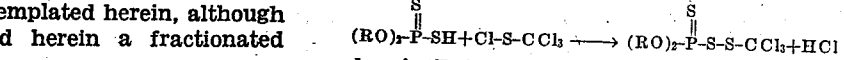


wherein R is alkyl or aralkyl. As contemplated herein, the dithiophosphoric acid may be substituted with two alkyl groups, two aralkyl groups, or an alkyl group and an aralkyl group. Di-substituted dithiophosphoric acids useful for the purposes of this invention may be prepared by any of the several methods of preparation known to the art, as for example, those described in the following publications: P. S. Pishchmuka, J. Russ. Phys. Chem. Soc. 56, 11 (1925) (C. A. 19, 2808 (1925)); P. S. Pishchmuka, J. Chim. Ukraine 1, 87 (1926) (C. A. 20, 2816 (1926)); Kovalevsky, Ann. 119, 303 (1861).

Contemplated also as a preferred reactant with perchloromethylmercaptan is a reaction product, predominantly comprised of a disubstituted dithiophosphoric acid, obtained by the reaction of an alcohol—specifically R.OH in which R is alkyl or aralkyl—and $P_2S_5$. Particularly preferred is that reaction product obtained by the reaction of four mols of said alcohol and one mol of $P_2S_5$. It will be seen, therefore, that the purposes of the present invention can be served by the use of a reaction product of perchloromethylmercaptan and either a pure disubstituted dithiophosphoric acid, as given by the formula above, or a crude reaction product predominantly comprised of a disubstituted dithiophosphoric acid.

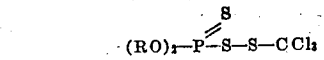
Typical alcohols represented by the formula R.OH in which R is alkyl or aralkyl are the following: methyl, ethyl, propyl, butyl, octyl (2-ethyl hexyl-), lauryl, oleyl, stearyl, monobutyl ether of diethylene glycol ("Butyl Carbitol"—which may be considered a substituted alcohol), benzyl, etc. Preferred, however, for the purposes of the present invention are methyl and butyl alcohols.

Although the mechanism of the reaction of perchloromethylmercaptan and a disubstituted dithiophosphoric acid is not yet thoroughly understood, it is probable that the reaction proceeds in the following manner:



wherein R is either alkyl or aralkyl. However, we do not wish to be bound by the theory of re-

action set forth above and the present invention is therefore not limited to compounds of the formula



but contemplates broadly the reaction products of perchloromethylmercaptan and disubstituted dithiophosphoric acids as described hereinabove.

The new and novel reaction products contemplated herein may be prepared in any of a number of ways known to those familiar with the art; preferred, however, is the detailed method given below by Example one.

## EXAMPLE ONE

### Reaction Products of Perchloromethylmercaptan and Dibutyl Dithiophosphoric Acid

*(A) Preparation of dibutyl dithiophosphoric acid*

Into a three-neck flask of suitable size, fitted with stirrer, reflux condenser and thermometer, were placed 1 part of $P_2S_5$, 1.27 parts of n-butyl alcohol and 1 part of carbon disulfide. The reaction was allowed to proceed at 30° C. for 1.5 hours and at 50° C. for the next 2 hours. The product was filtered and the solvent, along with any excess alcohol, was removed by topping at 90° C. with the aid of laboratory vacuum (about 200 mms.). The product was a yellow oil having a peculiar green cast. The theoretical neutralization number (N. N.) for dibutyl dithiophosphoric acid is 232; the neutralization number found for the product was 218.

(B) Into a three neck flask, fitted with stirrer, reflux condenser and dropping funnel, were placed 1.3 parts of dibutyl dithiophosphoric acid (prepared in A) and about 3 parts of low-boiling petroleum ether. During one hour, a solution of 1 part of perchloromethylmercaptan dissolved in about 3 parts of petroleum ether was slowly added. That the reaction proceeded smoothly was indicated by copious evolution of hydrogen chloride throughout the addition of perchloromethylmercaptan. When the addition was finished the mixture was stirred for 0.5 hour to complete the reaction. The petroleum ether solution was washed with sodium bicarbonate solution, with distilled water and then dried over sodium sulfate. The solvent was removed by distillation and the residue was topped, first with laboratory vacuum at 50° C., and then at 8–12 mm. at 80° C. The yield was 1.8 parts of a yellow, mobile oil which still contained traces of perchloromethylmercaptan. The product contained 23.1 per cent sulfur and 22.2 per cent chlorine.

As aforesaid, crude reaction products of an alcohol and $P_2S_5$ in which the predominant product is a disubstituted dithiophosphoric acid may be reacted with perchloromethylmercaptan to obtain reaction products which may be used for the purposes of this invention. Example two given below describes the preparation and properties, of a typical product which, as later demonstrated herein, is an effective Diesel fuel improving agent.

## EXAMPLE TWO

### Reaction Product of Perchloromethylmercaptan and Crude Dimethyl Dithiophosphoric Acid

*(A) Preparation of crude dimethyl dithiophosphoric acid*

Using the same procedure as described in Example one–A, a reaction product predominantly comprised of dimethyl dithiophosphoric acid was prepared from 1 part methanol and 1.74 parts of $P_2S_5$ with about 2 parts of carbon disulfide as the solvent. Calculated for dimethyl dithiophosphoric acid: N. N. 354: S, 40.5 per cent; found: N. N., 220: S, 28.1 per cent.

(B) The procedure in Example one (B) was followed in preparing the reaction product of perchloromethylmercaptan and crude dimethyl dithiophosphoric acid. As the acid was not miscible with petroleum ether, 1 part of the acid was added to a solution of 1.17 parts of perchloromethylmercaptan dissolved in about 3 parts of petroleum ether. The product contained 34 per cent sulfur and 21.4 per cent chlorine.

The effectiveness of the reaction products of perchloromethylmercaptan and disubstituted dithiophosphoric acids contemplated herein in improving the ignition qualities of Diesel fuels is demonstrated by comparatve results of a fuel blank and fuel blends. The ignition quality of the fuel and the fuel blends 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. 38, I, 392 (1938).)

The effectiveness of the new and novel reaction products contemplated herein is further demonstrated by comparison of fuel oil blends of typical reaction products with such blends of typical individual reactants, as for example, perchloromethylmercaptan, dibutyl dithiophosphoric acid and crude dimethyl dithiophosphoric acid. Perchloromethylmercaptan has previously been proposed as a Diesel fuel improving agent; however, as shown by the following data given in Table 1, this compound is much less effective than the reaction products contemplated herein.

The Diesel fuel oil used is a catalytically cracked number 2 fuel oil having the following characteristics.

| | |
|---|---|
| Gravity, °A. P. I. | 28.8 |
| Flash point (Pensky-Martens) °F. | 200 |
| Aniline point, °F. | 122 |
| A. S. T. M. distillation, °F: | |
| Initial | 431 |
| 10% | 467 |
| 90% | 582 |
| End point | 629 |
| Diesel index | 35.1 |
| Cetane number | 33.0 |

*Table 1*

| Substance blended with fuel | Per cent by wt. added | Cetane number of blend | Increase in cetane number |
|---|---|---|---|
| Perchloromethylmercaptan | 1.0 | 33.9 | 0.9 |
| Crude dimethyl dithiophosphoric acid | 1.0 | 35.5 | 2.5 |
| Dibutyl dithiophosphoric acid | 1.0 | 35.0 | 2.0 |
| Reaction product of perchloromethylmercaptan and crude dimethyl dithiophosphoric acid | 1.0 | 39.0 | 6.0 |
| Reaction product of perchloromethylmercaptan and dibutyl dithiophosphoric acid | 1.0 | 40.0 | 7.0 |

It will be readily observed from the foregoing results that the reaction products of per-

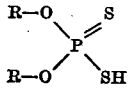
chloromethylmercaptan and disubstituted dithiophosphoric acids contemplated herein are effective to improve the ignition quality of a typical Diesel fuel, and are far superior in this regard to the individual reactants—perchloromethylmercaptan and typical disubstituted dithiophosphoric acids.

The term Diesel fuel, as used herein has reference to those non-viscous petroleum fractions, commonly denoted in the art as Diesel fuels, and to those hydrocarbon oils in general whose physical characteristics render them suitable for use as fuels in compression ignition engines.

The reaction products contemplated herein may be used in amounts ranging from 0.1 per cent to about 5.0 per cent, and it is to be understood that while we have herein described preferred procedures for preparing the same, the invention is not confined to products made by such procedure, but includes within its scope whatever charge or departures fairly come within the spirit of the appended claims.

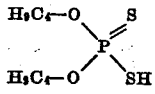
We claim:

1. An improved Diesel fuel comprising a hydrocarbon fuel oil and in admixture therewith a minor proportion of a reaction product obtained by the reaction of perchloromethylmercaptan with a compound selected from the group consisting of a dialkyl-dithiophosphoric acid, a diaralkyl-dithiophosphoric acid and an alkyl-aralkyl-dithiophosphoric acid, said compound being represented by the formula

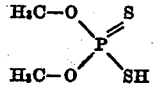


wherein R is selected from the group consisting of alkyl and aralkyl groups.

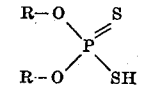
2. An improved Diesel fuel comprising a hydrocarbon fuel oil and in admixture therewith a minor proportion of the reaction product obtained by the reaction of perchloromethylmercaptan with dibutyl dithiophosphoric acid, said acid being represented by the formula



3. An improved Diesel fuel comprising a hydrocarbon fuel oil and in admixture therewith a minor proportion of the reaction product obtained by the reaction of perchloromethylmercaptan with dimethyl dithiophosphoric acid,

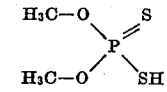


4. An improved Diesel fuel comprising a hydrocarbon fuel oil and in admixture therewith a minor proportion of the reaction product obtained by the reaction of perchloromethylmercaptan with the reaction product obtained by reaction of one mol of $P_2S_5$ and four mols of an alcohol, the latter reaction product being predominantly comprised of a disubstituted dithiophosphoric acid represented by the formula

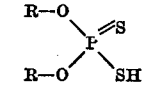


wherein R is selected from the group consisting of alkyl and aralkyl groups.

5. An improved Diesel fuel comprising a hydrocarbon fuel oil and in admixture therewith a minor proportion of the reaction product obtained by the reaction of perchloromethylmercaptan with the reaction product obtained by reaction of one mol of $P_2S_5$ and four mols of methyl alcohol, the latter reaction product being predominantly comprised of dimethyl dithiophosphoric acid represented by the formula

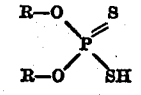


6. An improved Diesel fuel comprising a non-viscous petroleum oil and in admixture therewith a minor proportion, sufficient to decrease the ignition delay period of the fuel, of a reaction product obtained by the reaction of perchloromethylmercaptan with a compound selected from the group consisting of a dialkyl-dithiophosphoric acid, a diaralkyl-dithiophosphoric acid and an alkyl-aralkyl-dithiophosphoric acid, said compound being represented by the formula



wherein R is selected from the group consisting of alkyl and aralkyl groups.

7. An improved Diesel fuel comprising a non-viscous petroleum oil and in admixture therewith a minor proportion, from about 0.1 per cent to about 5.0 per cent, of a reaction product obtained by the reaction of perchloromethylmercaptan with a compound selected from the group consisting of a dialkyl-dithiophosphoric acid, a diaralkyl-dithiophosphoric acid and an alkyl-aralkyl-dithiophosphoric acid, said compound being represented by the formula



wherein R is selected from the group consisting of alkyl and aralkyl groups.

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