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DIESEL FUEL

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10 Claims. (Cl. 44—57)

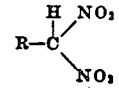
This invention relates to fuels for internal combustion engines of the Diesel or compression ignition type and is more particularly concerned with the improvement of such fuels by the addition thereto of a characterizing agent.

It is necessary for maximum efficiency of a Diesel engine that the ignition of the fuel be essentially instantaneous. Lack of coordination between the combustion and cylinder conditions or delayed ignition is the cause of the phenomenon known as "knocking." To rectify this condition it is desirable that the ignition delay period of the fuel be short. It is well known to those familiar with the art that the ignition quality of a Diesel or compression ignition fuel can be improved by the addition thereto of small amounts of certain compounds which accelerate ignition. By such means the better grades of Diesel fuel are improved. Similarly, the ignition quality of low-grade hydrocarbon mixtures may be improved sufficiently to make them available as fuels.

This invention is based upon the discovery that certain aliphatic dinitro compounds or dinitro paraffins are highly effective in improving the ignition quality of a Diesel fuel, and it contemplates Diesel fuel containing a minor proportion of such compounds for the aforesaid improvement and also contemplates the development of a method for accelerating the spontaneous ignition of liquid hydrocarbon fuels in compression ignition engines, which method is characterized by the admixture of these aliphatic dinitro compounds with the fuel prior to its ignition.

I am aware of the fact that mononitro paraffins have been proposed in U. S. Patent 1,820,983 for use in fuel oils for Diesel engines. I have discovered, however, that the degree of effectiveness of the dinitro paraffins is surprisingly superior to that of the mononitro paraffins, as is evident from the data hereinbelow described. U. S. Patent 1,820,983 also discloses an aryl dinitro compound, dinitro benzene, for use in this regard, but the patentee points out that the aryl dinitro compound possesses a relatively low degree of effectiveness.

As aforesaid, this invention is broadly directed to the use of aliphatic dinitro compounds to improve the ignition quality of Diesel fuel. More specifically, this invention is concerned with those dinitro paraffins which are characterized by an alkyl radical to which two nitro groups are attached to a single carbon atom, which compounds may be characterized by the general formula



wherein R is selected from the group consisting of hydrogen and alkyl radicals.

As typical examples of compounds contemplated herein are dinitro methane, dinitro ethane (specifically, 1,1-dinitro ethane), and dinitro heptane (specifically, 1,1-dinitro heptane). Additional examples contemplated herein are dinitro paraffins containing such alkyl groups as propyl, butyl, amyl, hexyl, etc., the dinitroparaffins containing such groups being dinitropropanes, dinitrobutanes, dinitropentanes, dinitrohexanes, etc., in which the two nitro groups are attached to a single carbon atom.

Various methods of preparing dinitro paraffins are known to those familiar with the art. Reference to the literature provides the following list of representative methods of preparation of such compounds. Other references may be available, and it is to be understood that the present invention is not concerned with or limited by the procedure by which the dinitro paraffins are prepared.

(*a*) By the oxidation of pseudonitroles with chromic acid. (See v. Meyer and Locher, Ann. 180, 133 (1876).)

(*b*) By the action of potassium nitrite and alcoholic potassium hydroxide on the bromonitro compound formed by the bromination of a nitro compound in alkaline solution. (See ter Meer, Ann. 181, 1 (1876).)

(*c*) By the action of concentrated nitric acid on certain ketones. (See M. G. Chancel, Bull. Soc. Chim. 31, (2) 504 (1879); M. Filesti and G. Ponzio, J. prakt. Chem. 55, (2) 195 (1879).)

The details in a typical procedure which may be employed in preparing the dinitro paraffins contemplated herein are illustrated in Example 1 below, which describes the preparation of 1,1-dinitro ethane according to the method of ter Meer referred to above.

Example 1

Into a three-neck flask fitted with stirrer, thermometer, and gas-inlet were placed 400 parts of water, 60 parts of sodium hydroxide, and 112.5 parts of nitroethane. Chlorine gas was led into the stirred solution until 107 parts by weight had been added. Enough cooling was provided to maintain the temperature at 15° C. The lower layer consisting of 1-chloro-1-nitroethane was separated, washed with water, dried and distilled. The amount of product boiling at 121–132° C. was 133 parts, which represents 83 per cent of the theoretical yield.

Sixty-five parts of the chloronitroethane obtained by the foregoing step were placed in a three-neck flask fitted with a stirrer, thermometer, and dropping funnel. Sixty parts of 85 per cent potassium nitrile, dissolved in 60 parts of

water, were added in one portion. To this stirred suspension were added 24 parts of sodium hydroxide in 300 parts of water at such a rate that the temperature remained at about 45° C. After standing 15 hours the mixture was acidified with 29.4 parts of sulfuric acid diluted with water. The oil which separated was taken up in ether and the aqueous portion extracted twice with ether. The combined extracts were dried over anhydrous sodium sulfate. The ether was then distilled and the residual oil topped to 50° C. vapor temperature at 190 mm. Hg. pressure. The yield was 41 parts or 58 per cent of the theoretical.

The effectiveness of the dinitro paraffins in improving the ignition quality of a Diesel fuel is demonstrated by comparative results of a fuel blank and a fuel blend obtained in the following manner: A base stock commonly known as number two fuel oil, which has a flash point of 172° F., A. P. I. gravity of 39.8, a cetane number of 55.0, and an aniline point of 160.5° F., was used in all tests. The ignition quality of the base stock 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 in a blend of cetane and alpha methyl naphthylene having the same combustion characteristics as the sample under test (see Proc. Am. Soc. Testing Materials, volume 36, I, 418 (1936)).

The results obtained in the foregoing tests with fuel blends containing various amounts of typical dinitro paraffins are tabulated in Table I below:

Table I

Compound added	Conc. wt.	Cetane No. of blend	Increase in cetane No.
	percent		
Dinitromethane	0.5	60.0	5.0
1,1-dinitroethane	1.0	67.0	12.0
1,1-dinitroethane	0.5	63.0	8.0
1,1-dinitroethane	0.25	59.0	4.0
1,1-dinitroheptane	1.0	58.0	3.0

From the foregoing results, it is seen that dinitro paraffins in amounts ranging from 0.25 per cent to 1.0 per cent increase the cetane number of the fuel described above from 3.0 to 12.0 units.

As previously mentioned, this invention is predicated upon the superiority of the dinitro paraffins over the mononitro paraffins. To demonstrate the superior effectiveness of the dinitro paraffins over the mononitro paraffins, typical mononitro paraffins were tested as improvers of ignition quality of the same base stock as described above. The results tabulated in Table II demonstrate clearly the superiority of the dinitro paraffins over the mononitro paraffins as improvers of ingnition quality of Diesel type fuels.

Table II

Compound added	Conc. wt.	Cetane No. of blend	Increase in cetane No.
	percent		
Nitromethane	1.0	55.0	0.0
Nitroethane	1.0	56.0	1.0
1-nitropropane	1.0	55.0	0.0
1-nitropropane	0.5	56.0	1.0
2-nitropropane	1.0	55.0	0.0
2-nitropropane	0.5	55.0	0.0
1-nitrobutane	1.0	52.5	−2.5
1-nitrobutane	3.0	54.5	−0.5

From comparison of Tables I and II above, it will be observed that the dinitroparaffins contemplated herein in amounts ranging from 0.25 per cent to 1.0 per cent effected improvement in the cetane number in amounts varying from 3.0 to 12.0 units, whereas the mononitro paraffins effected improvement in only two instances, where such increase was only 1.0 unit, and in two other instances actually decreased the cetane number, where such maximum decrease was 2.5 units.

The dinitro paraffins hereinafter claimed in this invention may be used in amounts varying from about 0.1 per cent to about 5.0 per cent, and it is to be understood that when the terms "Diesel fuel" or "Diesel-type fuel," etc., are used herein, I have reference to any liquid hydrocarbon adapted for use in any compression ignition engine.

I claim:

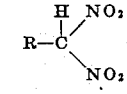
1. An improved Diesel fuel having in admixture therewith a minor proportion of a halogen-free dinitro paraffin wherein the two nitro groups are attached to a single carbon atom, said dinitro paraffin being present in sufficient amount to decrease the ignition delay period of the fuel.

2. An improved Diesel fuel having in admixture therewith between about 0.1 per cent and about 5.0 per cent of a halogen-free dinitro paraffin wherein the two nitro groups are attached to a single carbon atom, said dinitro paraffin being present to decrease the ignition delay period of the fuel.

3. An improved Diesel fuel having in admixture therewith a minor proportion of 1,1-dinitroethane in sufficient amount to decrease the ignition delay period of the fuel.

4. An improved Diesel fuel having in admixture therewith a minor proportion of 1,1-dinithroheptane in sufficient amount to decrease the ignition delay period of the fuel.

5. An improved Diesel fuel having in admixture therewith a minor proportion of a halogen-free dinitro paraffin which is characterized by the general formula:

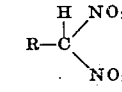


wherein R is selected from the group consisting of hydrogen and alkyl radicals.

6. The method of accelerating the ignition of a liquid hydrocarbon fuel in an engine where the fuel is injected into compressed air in the engine cylinder and ignites spontaneously therein, which comprises admixing with the fuel, prior to its injection into the cylinder, a minor proportion of a halogen-free dinitro paraffin wherein the two nitro groups are attached to a single carbon atom.

7. An improved Diesel fuel having in admixture therewith a minor proportion of a halogen-free dinitroheptane wherein the two nitro groups are attached to a single carbon atom, in sufficient quantity to decrease the ignition delay period of the fuel.

8. An improved Diesel fuel having in admixture therewith between about 0.1 per cent and about 5.0 per cent of a halogen-free dinitro paraffin which is characterized by the general formula:



wherein R is selected from the group consisting of hydrogen and alkyl radicals.

9. The method of accelerating the ignition of a

liquid hydrocarbon fuel in an engine where the fuel is injected into compressed air in the engine cylinder and ignites spontaneously therein, which comprises admixing with the fuel, prior to its injection into the cylinder between about 0.1 per cent and about 5.0 per cent of a halogen-free dinitro paraffin wherein the two nitro groups are attached to a single carbon atom.

10. An improved Diesel fuel having in admixture therewith a minor proportion, sufficient to decrease the ignition delay period of the fuel, of a halogen-free dinitropropane wherein the two nitro groups are attached to a single carbon atom.

JOHN H. McCRACKEN.

CERTIFICATE OF CORRECTION.

Patent No. 2,387,279. October 23, 1945.

JOHN H. McCRACKEN.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 60, Example I, for "nitrile" read --nitrite--; page 2, first column, line 62, for "ingnition" read --ignition--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of March, A. D. 1946.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.