

UNITED STATES PATENT OFFICE

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DIESEL FUELS

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This invention has to do with fuels for internal combustion engines of the Diesel or compression ignition type, and, more particularly, has to do with the improvement of such fuels by the addition thereto of a characterizing ingredient.

In order that the Diesel engine may be operated at maximum efficiency, ignition of the fuel should be essentially instantaneous. Delayed ignition or poor coordination between the combustion and cylinder conditions is the cause of "knocking" in Diesel engine operation. As is well known to those familiar with the art, this condition may be remedied by adding small amounts of certain materials or compounds to Diesel or compression ignition fuels. Compounds possessed of such characterizing ability accelerate the ignition of the fuel and, thus, provide a means whereby the ignition delay period of the fuel is rendered extremely short. In this way, the better grades of Diesel fuels are enhanced and low-grade hydrocarbon mixtures are so improved in ignition quality that they may be used as fuels.

This invention is based upon the discovery that nitrolic acids and pseudonitroles are effective in improving the ignition quality of Diesel fuel when used therein in small amounts. Accordingly, the present invention contemplates Diesel fuel containing a minor proportion of a nitrolic acid, or of a pseudonitrole, for the aforesaid improvement. The present invention also contemplates the development of a method for accelerating the spontaneous ignition of a liquid hydrocarbon fuel in compression ignition engines, said method being characterized by the admixture of a nitrolic acid, or of a pseudonitrole, with the fuel prior to its ignition.

The Diesel fuel improving agents contemplated herein are represented by the following general formulae:

Nitrolic acids	Pseudonitroles
$\begin{array}{c} \text{NO}_2 \\ \\ \text{R}-\text{C}=\text{NOH} \end{array}$	$\begin{array}{c} \text{NO}_2 \\ \\ \text{R}'-\text{C}-\text{R}'' \\ \\ \text{NO} \end{array}$

wherein R is a hydrogen atom or a hydrocarbon radical, such as an alkyl, aryl, aralkyl, or alkaryl radical; R' and R'' are hydrocarbon radicals, such as alkyl, aryl, aralkyl, or alkaryl radicals and

may be the same or different radicals. Typical of the nitrolic acids are methyl, ethyl, propyl, phenylmethyl, and tolylmethyl nitrolic acids. Illustrative pseudonitroles are propyl, butyl, phenylmethyl, and xylylmethyl pseudonitroles. Particular preference is given herein to propyl nitrolic acid and to propyl pseudonitrole.

The pseudonitroles represented by the foregoing general formulae apparently exist in a monomeric form and in a dimeric form. For example, propyl pseudonitrole is a white solid in the dimeric form, whereas the monomer is a blue liquid. We have found that the monomer of propyl pseudonitrole is more soluble than the dimer in a non-viscous petroleum oil. We have also found that the more oil-soluble monomer can be obtained substantially free of the dimer by using a hydrocarbon oil diluent in the procedures referred to hereinafter. In this way, the more desirable form of the Diesel fuel improving agents contemplated herein, is obtained. It is to be understood, however, that both the more oil-soluble monomeric forms and the less oil-soluble dimeric forms of pseudonitroles are contemplated by the present invention.

Several methods of preparation of nitrolic acids and pseudonitroles are known to those skilled in the art. In general, these methods involve the reaction of a primary or a secondary nitro-paraffin with nitrous acid at a temperature less than about 10° C. Detailed descriptions of such methods are provided in the chemical literature, as in Annalen 175, 114 (1875) and 175, 120 (1875). Recently a novel procedure for the preparation of these compounds has been developed. In this latter procedure, a nitrolic acid is prepared from a primary nitroparaffin, aqueous alkali hydroxide and mineral acid (other than nitrous acid) at a temperature below about 10° C. Similarly, in this procedure, a pseudonitrole is obtained from a secondary nitroparaffin, said alkali and said acid at a temperature below about 10° C. It will be apparent that while nitrous acid or alkali nitrite is not used in this recently developed procedure, the equivalent of nitrous acid or alkali nitrite is formed therein and reacts to introduce a nitroso group (—NO) into the desired compounds.

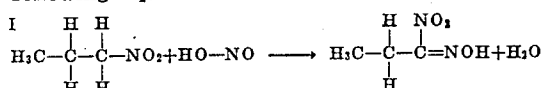
As an example of the nitrolic acids, we have prepared propyl nitrolic acid by a method similar to that described in Annalen 175, 114 (1875), and to illustrate the pseudonitroles we have prepared

propyl pseudonitrole by a method similar to that described in Annalen 175, 120 (1875).

EXAMPLE I

Propyl nitrolic acid

The reaction involved in the method of preparation described below is represented by the following Equation I:

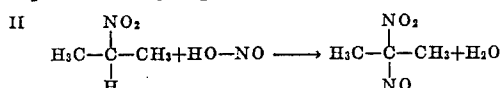


Twenty-two grams (0.25 mole) of 1-nitropropane were placed in a reaction flask equipped with a stirrer, thermometer and dropping funnel, and surrounded by an ice bath. A 10% solution of sodium hydroxide, 110 grams, was added slowly, care being taken to keep the temperature below about 10° C. After all of the 1-nitropropane had dissolved in the alkali solution, 20 grams of sodium nitrite were added slowly to the solution. When the nitrite had dissolved therein, cold, dilute hydrochloric acid was added dropwise to the solution at approximately 5° C. The reaction mixture turned dark red at first but became lighter in color as more acid was added. Addition of acid required about 2 hours and was continued until the reaction mixture was light blue-green in color. The blue-green reaction mixture was then made alkaline with dilute sodium hydroxide solution and reacidified with dilute hydrochloric acid. After repeating this last-mentioned operation three times, the slightly acid reaction mixture was extracted three times with successive portions (80 cc. each) of ether. The ether extract thus obtained was filtered and the ether allowed to evaporate spontaneously. Upon evaporation of the ether, propyl nitrolic acid was obtained as a mixture of white crystals (M. Pt. 59-60° C.) and a yellow oil. The yield was 15 grams or 51% of the theoretical.

EXAMPLE II

Propyl pseudonitrole

The reaction between a secondary nitro-paraffin, as 2-nitropropane, and nitrous acid is represented by Equation II:



Twenty-five grams (0.36 mole) of 2-nitropropane were added slowly to solution of 20 grams of potassium hydroxide in about 150 cc. of water. The mixture thus formed was kept in a tightly stoppered flask, which was immersed in an ice bath to prevent a rise in temperature. The flask was shaken from time to time to aid in dissolving the nitro compound. When the 2-nitropropane had dissolved, 21 grams of sodium nitrite were added and dissolved. The solution was then poured into a flask equipped with stirrer, thermometer and dropping funnel. This flask was surrounded with an ice bath to maintain a low temperature within said flask. Concentrated sulfuric acid, 70 grams, diluted with ice water, was added slowly at a temperature below 10° C. As the acid was added, the solution turned blue and a pale blue solid began to separate. When all of the acid had been added, the solid was filtered off on a Buchner funnel, then washed with dilute potassium hydroxide and finally with cold water. The pale blue solid, which was propyl pseudonitrole, was then dried

and weighed. The yield was 23 grams or 70% of the theoretical.

The effectiveness of the nitrolic acids and pseudonitroles in improving the ignition qualities of Diesel fuel is demonstrated by comparative test results of a fuel blank and of a fuel blend. The fuel used in the tests described hereinafter was a representative Diesel fuel known in the art as a catalytically cracked number two fuel oil. This fuel had the following characteristics:

Specific gravity	0.8833
A. P. I. gravity	28.7
Color (Lovibond)	9
Sulfur	0.2 percent
Pour point	5 °F.
Flash point	220 °F.
Aniline No.	125
Diesel index	35.9
Cetane number	33.0
A. S. T. M. distillation, °F.:	
Initial	431
10%	481
90%	589
End point	633

The ignition quality of the fuel and 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 alphamethyl naphthalene having the same combustion characteristics of the sample under test (Reference: Proc. Amer. Soc. Testing Materials, vol. 36, I, 418 (1936)).

The results obtained in the foregoing tests with fuel blends containing small amounts of propyl nitrolic acid and of propyl pseudonitrole, both of which are typical of the Diesel fuel improving agents contemplated herein, are set forth in the table below:

Table

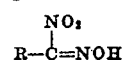
Compound blended with base fuel	Conc., wt. per cent	Cetane number of blend	Increase in cetane number
Propyl nitrolic acid	2	37.4	4.4
Do	1	37.1	4.1
Propyl pseudonitrole	1	37.5	4.5

For the purposes of this invention, the nitrolic acids and pseudonitrole represented by the general formula shown hereinabove may be used in amounts of from about 0.1 per cent to about 5.0 per cent.

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

We claim:

1. An improved Diesel fuel comprising a non-viscous hydrocarbon oil and in admixture therewith a minor proportion, sufficient to improve the ignition quality of the fuel, of a compound selected from the group consisting of a nitrolic acid and a pseudonitrole, said nitrolic acid being represented by the general formula

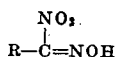


wherein R represents a radical selected from the group consisting of hydrogen, and alkyl, aryl, aralkyl and alkaryl radicals, and said pseudonitrole being represented by the general formula



wherein R' and R'' represented radicals selected from the group consisting of alkyl, aryl, aralkyl and alkaryl radicals.

2. An improved Diesel fuel comprising a non-viscous hydrocarbon oil and in admixture therewith a minor proportion, from about 0.1 per cent to about 5.0 per cent, of a compound selected from the group consisting of a nitrolic acid and a pseudonitrole, said nitrolic acid being represented by the general formula

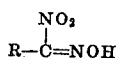


wherein R represents a radical selected from the group consisting of hydrogen, and alkyl, aryl, aralkyl and alkaryl radicals, and said pseudonitrole being represented by the general formula



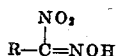
wherein R' and R'' represent radicals selected from the group consisting of alkyl, aryl, aralkyl and alkaryl radicals.

3. An improved Diesel fuel comprising a non-viscous hydrocarbon oil and in admixture therewith a minor proportion, sufficient to improve the ignition quality of the fuel, of a nitrolic acid represented by the general formula



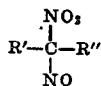
wherein R represents a radical selected from the group consisting of hydrogen and alkyl, aryl, aralkyl and alkaryl radicals.

4. An improved Diesel fuel comprising a non-viscous hydrocarbon oil and in admixture therewith a minor proportion, from about 0.1 per cent to about 5.0 per cent, of a nitrolic acid represented by the general formula



wherein R represents a radical selected from the group consisting of hydrogen and alkyl, aryl, aralkyl and alkaryl radicals.

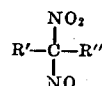
5. An improved Diesel fuel comprising a non-viscous hydrocarbon oil and in admixture therewith a minor proportion, sufficient to improve the ignition quality of the fuel, of a pseudonitrole represented by the general formula



wherein R' and R'' represent radicals selected from the group consisting of alkyl, aryl, aralkyl and alkaryl radicals.

6. An improved Diesel fuel comprising a non-viscous hydrocarbon oil and in admixture therewith a minor proportion, from about 0.1 per cent

to about 5.0 per cent, of a pseudonitrole represented by the general formula



wherein R' and R'' represent radicals selected from the group consisting of alkyl, aryl, aralkyl and alkaryl radicals.

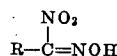
7. An improved Diesel fuel comprising a non-viscous hydrocarbon oil and in admixture therewith a minor proportion, sufficient to improve the ignition quality of the fuel, of propyl nitrolic acid.

8. An improved Diesel fuel comprising a non-viscous hydrocarbon oil and in admixture therewith a minor proportion, from about 0.1 per cent to about 5.0 per cent, of propyl nitrolic acid.

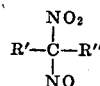
9. An improved Diesel fuel comprising a non-viscous hydrocarbon oil and in admixture therewith a minor proportion, sufficient to improve the ignition quality of the fuel, of propyl pseudonitrole.

10. An improved Diesel fuel comprising a non-viscous hydrocarbon oil and in admixture therewith a minor proportion, from about 0.1 per cent to about 5.0 per cent, of propyl pseudonitrole.

11. The method of accelerating the ignition quality of a liquid hydrocarbon fuel in an engine where the fuel is injected into the engine cylinder and ignites spontaneously therein, which comprises admixing with the fuel prior to its ignition in the cylinder, a minor proportion of a compound selected from the group consisting of nitrolic acid and a pseudonitrole, said nitrolic acid being represented by the general formula

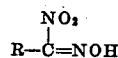


wherein R represents a radical selected from the group consisting of hydrogen and alkyl, aryl, aralkyl and alkaryl radicals, and said pseudonitrole being represented by the general formula



wherein R' and R'' represent radicals selected from the group consisting of alkyl, aryl, aralkyl and alkaryl radicals.

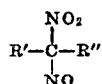
12. The method of accelerating the ignition quality of a liquid hydrocarbon fuel in an engine where the fuel is injected into the engine cylinder and ignites spontaneously therein, which comprises admixing with the fuel, prior to its ignition in the cylinder, a minor proportion of a nitrolic acid represented by the general formula



wherein R represents a radical selected from the group consisting of hydrogen and alkyl, aryl, aralkyl and alkaryl radicals.

13. The method of accelerating the ignition quality of a liquid hydrocarbon fuel in an engine where the fuel is injected into the engine cylinder and ignites spontaneously therein, which comprises admixing with the fuel, prior to its ignition in the cylinder, a minor proportion of

a pseudonitrole represented by the general formula



wherein R' and R'' represent radicals selected from the group consisting of alkyl, aryl, aralkyl and alkaryl radicals.

14. The method of accelerating the ignition quality of a liquid hydrocarbon fuel in an engine where the fuel is injected into the engine cylinder and ignites spontaneously therein,

which comprises admixing with the fuel, prior to its ignition in the cylinder, a minor proportion of propyl nitrolic acid.

15. The method of accelerating the ignition quality of a liquid hydrocarbon fuel in an engine where the fuel is injected into the engine cylinder and ignites spontaneously therein, which comprises admixing with the fuel, prior to its ignition in the cylinder, a minor proportion of propyl pseudonitrole.

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