Patented Dec. 24, 1940 2,226,298

UNITED STATES PATENT OFFICE

2,226,298

METHOD AND COMPOSITION FOR IMPROVING DIESEL FUEL IGNITION

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No Drawing. Application May 16, 1939, Serial No. 274,030

16 Claims. (Cl. 44—9)

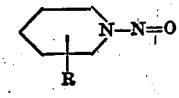
This invention relates to fuels for internal combustion engines of the Diesel type, and it has particularly to do with the addition to liquid petroleum fuels of certain substances designed to control the combustion characteristics of the fuels.

In Diesel engine operation, a liquid fuel is injected into a combustion chamber and ignited by compression. In the attainment of minimum engine knocking, the time interval between the instant of injection and the instant of ignition, referred to as the "delay period," should be as brief as possible. Generally, this delay period is known to be affected by the type or character of the hydrocarbons composing the fuel; also, it may be shortened by the addition of ignition accelerators or primers to the fuel, and various nitrates, nitrites and organic peroxides are known to be effective for this purpose. Occasionally, but not invariably, the addition of a substance found to act as an efficient primer during continuous running will also act to assist in the cold starting of the motor.

It has been found that the addition of small amounts of petroleum nitrogen base nitrosoamines to a Diesel fuel shortens the period of delay between injection and ignition and, in addition, enables the motor to be started at a relatively lower temperature under a given set of motor conditions. These substances are non-explosive in themselves, have low vapor pressures and are sufficiently soluble in oil; their manufacture and introduction to a hydrocarbon fuel is attended by no hazard; the fuels prepared by their addition are stable in storage; and their addition imparts no objectionable odor or other adverse characteristics from the standpoint of salability. When introduced into the air intake manifold of the motor, in amounts somewhat higher than those provided in a fuel adapted for continuous running, the petroleum nitrogen base nitrosoamines materially enhance cold starting.

It is accordingly an object of the invention to disclose and provide superior fuels of the Diesel type, comprising petroleum hydrocarbon fuels of suitable boiling range, containing small amounts of petroleum nitrogen base nitrosoamines. It is another object of the invention to disclose Diesel fuels of enhanced combustion characteristics, capable of smooth operation at minimum knocking and with minimum delay periods, which are low in cost, stable in storage, without hazard in preparation or handling. It is another object to provide methods of utilizing the petroleum nitrogen base nitrosoamines in the cold starting of Diesel motors by providing for their introduction to the motor in somewhat higher concentrations than suffice for highly efficient continuous running. Other objects, uses and advantages of the invention will be apparent to those skilled in the art to which it appertains.

The petroleum nitrogen base nitrosoamines added to a Diesel type fuel for the purposes of this invention correspond to the following type structure:



in which R represents an alkyl side chain of two or more carbon atoms. In the above type structure, R may be attached to the beta-carbon atom in the heterocyclic ring, but it is to be understood that R may be attached in other positions on the ring and that more than a single alkyl side chain of two or more carbon atoms per chain may exist on the same ring. In the above type structure, the heterocyclic ring may contain one or two unsaturated carbon-to-carbon bonds, but saturation will usually be complete.

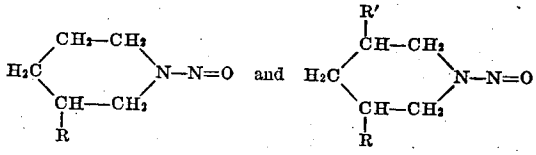
The petroleum nitrogen base nitrosoamines, added to Diesel type fuels for the purposes of the invention, may be prepared in accordance with the following exemplary procedures:

A crude cracked naphtha, as obtained in the pyrogenetic cracking of a nitrogen-containing crude petroleum oil or distillate, is extracted at ordinary temperatures with dilute aqueous sulfuric acid, of a concentration generally below about 50% H_2SO_4 and preferably about 30% H_2SO_4; water-soluble sulfates of mixed petroleum nitrogen bases are formed. The petroleum nitrogen bases are recovered by neutralization with a dilute aqueous alkali metal hydroxide solution, and they are sufficiently water-insoluble to permit of stratification and decantation. In a typical case, a mixture of the crude bases thus separated from a crude cracked 100°–500° F. naphtha of California petroleum origin had a specific gravity of 0.9370, a dissociation constant of 4×10^{-8}, an average molecular weight of about 146, and an A. S. T. M. distillation boiling range between 340° and 444° F. (5% point, 394°; 90% point, 418° F.). After such recovery, the petroleum nitrogen bases are reduced to secondary amines, and such reduction may be accomplished by metallic sodium in alcoholic solution, electrolytically in dilute acid solution, or by hydrogenation under pressure in the presence of a suitable catalyst. In the latter method of reduction, MoS_3 deposited

on charcoal may be the catalyst, and mol ratios of hydrogen to nitrogen base between 10 to 1 and 50 to 1 may be employed, at pressures up to 200 atmospheres; CS_2 or an analogous sulfur-carrier should be introduced, as $(NH_4)_2S$ is formed during the reduction and desulfurization of the catalyst may prejudice the recovery of high yields of the reduced bases. The temperature of hydrogenation should be between 475° and 535° F.; 500° F. is a good average, and the temperature should not exceed 535° F. A suitable space rate is 0.3 volume of liquid charged/hour/volume of catalyst. In a typical reduction of nitrogen bases by such a hydrogenation, 56% of the bases were reduced to secondary amines, 7% were decomposed and 37% were unreduced or reacted upon. After reduction, whether electrolytically, by metallic sodium or by hydrogenation, the secondary amines are recovered from the reaction product mixture by adjustment of pH to 9.5, in aqueous solution by addition of acid: unreduced nitrogen bases remain water-insoluble, while the reduced bases by reason of their higher basicity pass into water solution as salts. In the above typical case, a mixture of the petroleum nitrogen bases thus reduced (in their free form) had a specific gravity of 0.8708, a dissociation constant of 1×10^{-3}, an average molecular weight of 150, and an A. S. T. M. distillation boiling range between 330° and 450° F.

Subsequent to the reduction of the petroleum nitrogen bases to secondary amines, the nitroso derivatives are prepared in the usual manner by the addition of a nitrite to the cold aqueous acid solution of the amine salts.

In a sequence of steps such as that outlined, a mixture of petroleum nitrogen base nitrosoamines was recovered which had a specific gravity of 0.995, originally a yellow liquid but darkening to a red brown on standing. The substance or mixture of substances, as obtained, had an average molecular weight of about 179 and a nitrogen content of about 15.6%. From the various reactions of these substances and from those of the nitrogen bases originally employed in their derivation, it appears that the heterocyclic ring may be completely saturated and that, as an average for an apparent series, one 5-carbon atom chain or a 2-carbon atom and a 3-carbon chain may be attached to the same ring in the beta- or beta-beta positions. Thus the probable structural types are



where R and R′ are alkyl groups containing 2 or more carbon atoms (in the above typical case R and/or R+R′ contain an average of about 5 carbon atoms per molecule, and the individuals making up the series thus carry chains of 2 to 6, 7 or 8 carbon atoms per chain).

By the addition of these nitrosoamine derivatives of petroleum nitrogen bases to Diesel type fuels, in amounts between about 0.1% and about 10% by weight (generally amounts between about 0.25% and about 5.0% by weight will be found most satisfactory in practice), the "cetane number" of the fuel is considerably raised, "cetane number" rise being indicative of a decrease in delay period between injection and ignition in the motor combustion chamber, as exemplified by the following:

Rise in cetane number of fuel with addition of nitrosoamine derivatives of petroleum nitrogen bases

0.1%	0.25%	0.5%	1.0%	2.0%	5.0%
4	6	9	13	17	29

The above additions of the exemplified nitrosoamine derivatives of reduced petroleum nitrogen bases were all made to the same base Diesel fuel, and the determinations of cetane number were all made in the same standardized engine under closely controlled and accurately duplicable conditions. The cetane number of the base fuel itself was 39, when tested under the same conditions.

The cetane number determinations given herein are determined by a procedure known as the Standard Oil Company of California delay method, in which the ignition delay with combustion occurring at top dead center is utilized as the test criterion and in which the operating variable is the injection advance equivalent to the ignition delay when firing is made to occur at top dead center. In brief, this procedure is characterized as follows: The fuel to be tested is introduced into the engine and the injection is then advanced or retarded until firing occurs at top center; the ignition delay is read and recorded. The procedure is then repeated for a series of cetane-alphamethylnaphthalene blends which produce greater and lesser ignition delays than the fuel under test. A plot is made of the ignition delays of the cetane-alphamethylnaphthalene blends in terms of the percentage of cetane in the blends. The ignition delay of the fuel under test is placed on this plot and its corresponding cetane number is determined. The method may be employed in a Fairbanks Morse or other service engine capable of sufficient control of all operation variables. The method correlates well with service performance.

The addition of the above and analogous nitrosoamine derivatives of petroleum nitrogen bases to Diesel fuel stocks of higher and of lower original cetane number causes rises comparable to those exemplified.

In general, it may be said that a rise in cetane number of 2.0, caused by the addition of 1% by weight of a Diesel fuel "primer" is significant and valuable.

Further, the presence of these nitrosoamine derivatives of reduced nitrogen bases in Diesel fuels is of advantage in the cold starting of Diesel motors.

Generally, under given conditions of starting, the minimum temperature at which the engine will fire and continue to operate, on an uncompounded petroleum hydrocarbon fuel, depends upon the delay cetane number of the fuel, and it is lowered relative to a rise in delay cetane number. It has been found that the presence of these nitrosoamine derivatives of reduced petroleum nitrogen bases in a hydrocarbon fuel of the Diesel type causes a lowering in the temperature of cold starting, in degrees Fahrenheit, about equivalent to the cetane number rise caused by their presence. Such an effect is by no means generally true of substances found to cause cetane number rise upon addition to hydrocarbon fuels: for ex-

ample, ethyl nitrate, effective to cause cetane number rise, causes little or no lowering of the temperature of cold starting; likewise nitrosopiperidine, at first sight apparently analogous to the substances here disclosed, causes no lowering of the temperature of cold starting, although it is effective to cause cetane number rise.

The procedure employed in determining the starting qualities of the Diesel fuels of this invention, exemplified above as causing a lowering in temperature of cold starting, in degrees Fahrenheit, about equivalent to cetane number rise brought about by the addition of these nitrosoamine derivatives of petroleum nitrogen bases, is referred to as the Standard Oil Company of California cold starting method, and utilizes the ambient temperature allowing a starting just 5 seconds subsequent to cranking as the test criterion. In brief, this procedure is characterized as follows: The fuel to be tested is introduced into the fuel system, the jacket and intake air temperatures are established with the engine stopped, and the engine is then cranked at 280 R. P. M. until firing occurs. The time interval between first injection of the fuel and the first firing explosion is measured and recorded as the cranking time. The procedure is repeated with the jacket and intake air temperature either raised or lowered as required to result in starting with just 5 seconds of cranking. This final temperature is recorded as the ambient starting temperature of the fuel. A Caterpillar engine is employed under service conditions, and the starting temperature determinations are representative of field performance.

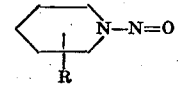
For example, an uncompounded, highly naphthenic (California) Diesel distillate fuel would not permit the test engine to start at temperatures below 36° F. The addition of 1.0% of the nitrosoamine derivatives of reduced petroleum nitrogen bases, prepared as described and exemplified hereinabove, to this same fuel, allowed the engine to start at 27° F. under the test conditions.

Under certain more unusual conditions, for example in cold starting at very low temperatures, in accelerating starting at ordinary temperatures, and in operations with hydrocarbon fuels of low cetane number, it has been found advantageous to introduce more than the already disclosed small amounts of the reduced nitrogen base nitrosoamines (based on the hydrocarbon fuel components), sometimes for brief periods only. This may be done by controlled introduction of the nitrosoamine derivatives to the air intake manifold or stream to the motor, either with or without the presence of the usual small amounts of these substances in the fuel introduced in the liquid injection system. Such air intake introduction obviates the difficulty of purging the regular fuel system and provides for discontinuous addition for special sets of circumstances. It may be accomplished by addition of these nitrosoamine derivatives through the intake air pipe or a by-pass on the same, as desirable, in finely divided spray form, for example by air aspiration through a jet nozzle from a flow line appropriately calibrated or supplied from a chamber with suitable calibration. By reason of the low vapor pressure and volatility of these substances, and because of the difficulties of securing fine dispersion in accurately measured quantities, it is preferable to supply to the air intake stream a solution or suspension of the reduced nitrogen base nitrosoamines rather than the substances themselves: solutions or suspensions containing 10% or more by weight of these substances, in a hydrocarbon fuel of the gasoline or Diesel fuel boiling range or a combustible or non-combustible liquid such as carbon tetrachloride, carbon bisulfide or chloroform, an ether such as ethyl, isopropyl or a higher ether or alcohol, or mixtures of such ethers and/or other solvents, are suitable for this purpose; a mixture of 10% up to 50 or more per cent of these substances in the Diesel fuel ordinarily employed in the continuous running of the motor is particularly advantageous. Such air stream introduction, in the manner described, provides a high concentration of these ignition accelerators in the combustion chamber of the motor, the ratio of the substance to the hydrocarbon fuel normally entering through the liquid injection system being suitably from 20:1 to 35:1 for the desired short periods; ratios of the nitrosoamines to hydrocarbon fuel oil as high as 50:1 and as low as 1:20 may be employed in operations of this character. Discontinuous additions at other than starting times may occasionally be of advantage with this air intake method of introduction.

The term "Diesel fuel" as used herein has particular reference to petroleum distillates of kerosene and light gas oil boiling range, but the term is intended to include as well both the slightly more and the slightly less volatile distillates which are designed for ordinary use in internal combustion engines of the Diesel type.

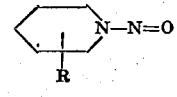
I claim:

1. An improved Diesel fuel comprising a hydrocarbon fuel oil containing between about 0.1% and about 10% by weight of an organic compound of the type structure



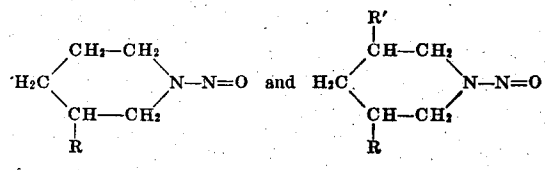
in which R represents at least one alkyl side chain of 2 or more carbon atoms per chain and in which the heterocyclic ring may be saturated or may contain one or two unsaturated carbon-to-carbon bonds.

2. An improved Diesel fuel comprising a hydrocarbon fuel oil containing between about 0.1% and about 10% by weight of an organic compound of the type structure



in which R represents at least one alkyl side chain of more than 2 carbon atoms per chain.

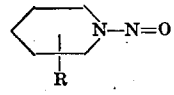
3. An improved Diesel fuel comprising a hydrocarbon fuel oil containing between about 0.1% and about 10% by weight of an organic compound selected from the group consisting of the types



in which R and R' are alkyl groups containing 2 or more carbon atoms per group.

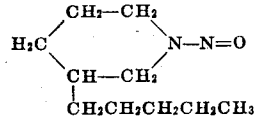
4. An improved Diesel fuel comprising a hydrocarbon fuel oil containing between about 0.25%

and about 5.0% by weight of an organic compound of the type structure



in which R represents at least one alkyl side chain of more than 2 carbon atoms per chain.

5. An improved Diesel fuel comprising a hydrocarbon fuel oil containing between about 0.1% and about 10% by weight of an organic compound of the structure



6. An improved Diesel fuel comprising a hydrocarbon fuel oil containing a minor proportion, sufficient to decrease the ignition delay period of the fuel, of a nitroso derivative of reduced cracked petroleum naphtha nitrogen bases.

7. An improved Diesel fuel comprising a hydrocarbon fuel oil containing between about 0.1% and about 10% by weight, sufficient to decrease the ignition delay period of the fuel, of a nitroso derivative of reduced cracked petroleum naphtha nitrogen bases.

8. An improved Diesel fuel comprising a hydrocarbon fuel oil containing between about 0.25% and about 5.0% by weight, sufficient to decrease the ignition delay period of the fuel, of a nitroso derivative of reduced cracked petroleum naphtha nitrogen bases.

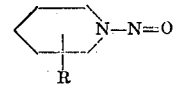
9. An improved Diesel fuel comprising a hydrocarbon fuel oil containing a minor proportion, sufficient to decrease the ignition delay period of the fuel, of an ignition accelerator derived from cracked petroleum naphtha nitrogen bases by the process which comprises: reducing petroleum nitrogen bases to secondary amines, removing from the secondary amines the major proportion of unreduced petroleum nitrogen bases and reacting the petroleum nitrogen base secondary amines with sodium nitrite to form the corresponding nitroso derivatives of the reduced petroleum nitrogen bases.

10. An improved Diesel engine ignition accelerating composition comprising nitroso derivatives of reduced petroleum nitrogen bases in admixture with a liquid diluent, the said composition containing at least 0.1% by weight of the said nitroso derivatives.

11. An improved Diesel engine ignition accelerating composition comprising nitroso derivatives of reduced petroleum nitrogen bases in admixture with a liquid diluent, the said composition containing at least 10% by weight of the said nitroso derivatives.

12. An improved Diesel engine ignition accelerating composition comprising nitroso derivatives of reduced petroleum nitrogen bases in admixture with a liquid diluent, the said composition containing more than 50% by weight of the said nitroso derivatives.

13. The method of accelerating the ignition of Diesel cycle internal combustion engines which comprises admixing with the fuel, prior to ignition, a minor proportion of an organic compound of the type structure



in which R represents an alkyl side chain of more than 2 carbon atoms and in which the heterocyclic ring may contain one or two unsaturated carbon-to-carbon bonds.

14. The method of accelerating the ignition of a Diesel cycle internal combustion engine which comprises introducing nitroso derivatives of reduced petroleum nitrogen bases into the combustion chamber of the engine, simultaneously with the introduction thereto of a hydrocarbon Diesel fuel.

15. The method of accelerating the ignition of a Diesel cycle internal combustion engine which comprises introducing nitroso derivatives of reduced petroleum nitrogen bases into the intake manifold of the engine, simultaneously with the introduction of a hydrocarbon Diesel fuel to the combustion chamber of the said engine.

16. The method of accelerating the ignition of a Diesel cycle internal combustion engine which comprises introducing nitroso derivatives of reduced petroleum nitrogen bases in a diluent to the air intake manifold of the engine, simultaneously with the introduction of a hydrocarbon Diesel fuel to the combustion chamber of the said engine.

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