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DIESEL FUEL IGNITION ACCELERATOR

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7 Claims. (Cl. 44-9)

This invention relates to an improvement of hydrocarbon fuels by addition compounds serving to accelerate their ignition in compression-ignition engines chiefly of the high speed type, commonly known as Diesel engines.

The beneficial action of addition compounds which shorten the delay period between injection of a fuel and its ignition effected spontaneously with compressed air in a Diesel engine is well known. A number of addition compounds have been proposed for this general purpose. Among the most effective compounds heretofore recommended to function as ignition accelerators of hydrocarbon Diesel fuels are organic nitric and nitrous esters. To offset acid forming tendencies of such esters other compounds of more basic character have also been proposed, for example, some oximes and amines which, in general, are relatively less effective for inducing ignition of the fuel.

An object of the present invention is to improve Diesel fuels by normally stable oil-soluble addition compounds having base forming tendencies but with high effectiveness for accelerating ignition more comparable to that of alkyl nitrates. As a further object, this invention provides a method of modifying oxy-nitrogen groups characteristic of nitro, nitroso, and oximino compounds to obtain the improved Diesel fuel ignition accelerators.

It has now been found that alkylating or acylating aliphatic oximes and related compounds, particularly at the functional group, a marked improvement is made in their ignition accelerating action as well as in their oil solubility and stability in storage.

Aliphatic oximes are compounds containing the group



Other compounds similar in structure and behavior are isomeric forms of aliphatic nitro and nitroso compounds known as iso-nitroso and iso-nitro compounds. The oximes are generally regarded as derivatives of aldehydes and ketones, according to whether their structure is RCH:NOH or

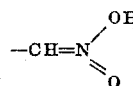


These structures are the same for the tautomeric and isomeric transformation products of pri-

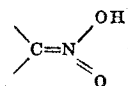
mary and secondary nitroso compounds, which contain groups $-\text{CH}_2\text{NO}$ and



Similarly, primary and secondary nitroparaffins are considered to assume the tautomeric and isomeric forms having the structures



or



It is well known that the majority of the described aliphatic oximino compounds are solid at room temperature, have low hydrocarbon oil solubility, and are in some instances water soluble.

By the action of alkylating agents, oximes are converted into ether oximes which dissolve in hydrocarbon oils with ease. The etherifying of the oximes, or alkylation of the oximino group, is readily attained by the use of reagents, such as dimethyl sulfate in the presence of caustic soda, alkyl iodides, or other known alkylating agents. An ether extraction may be made of the alkylation product to recover the desired final product having the type formula



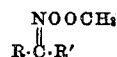
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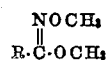
in which R, R', and R'', represent aliphatic groups, e. g., a methyl group, or homologous groups.

The term aliphatic radical, as used herein and in the claims, refers to open chain groups containing hydrogen and carbon, e. g., alkylene, alkyl, or acyl.

Of equivalent value are the ethers or esters in which R' or R'' is an acyl group, as in



or as in



These may be obtained, for example, by etherify-

ing acetyl aldoxime and by acylation of iso-nitro compounds. A general method for preparing the methyl ester oximes ($R \cdot CH:NO \cdot OCH_3$) involves the reaction of diazo methane with primary

nitro-paraffins behaving in the reaction as iso-nitro compounds.

It has been found that the esterified and etherified oximes are substances more soluble than the unmodified oximes in hydrocarbon oils.

Also, they have been observed to act more generally in a basic or neutral manner and are thus able to minimize the development of acidity more effectively.

There are a number of well known ways for obtaining compounds to be converted into ether or ester oximes. Some of the principal methods are outlined below:

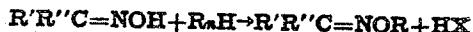
1. Aliphatic nitroso or nitro compounds which have strong tendencies to rearrange into oximes are obtained readily by reacting nitrous anhydride, nitric anhydride, or nitrosyl chloride with olefins, particularly branched olefins.

2. Ketones react with nitrous esters or with nitrous acid to form oximes (iso-nitroso-ketones).

3. Aldehydes and ketones react with hydroxyl amine to yield aldoximes and ketoximes.

Oximes can be formed from 1:2 and 1:4 diketones also from various hydroxy aldehydes and ketones, e. g., glycol aldehyde, aldol, acetyl carbinol, acetoin, etc.

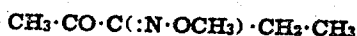
Starting with an oximino compound or compound capable of reacting as oximino compound regardless of its origin, the etherification of the oximino group ($=NOH$) is effected by the general reaction:



where the R groups represent aliphatic radicals and R_nH represents an alkylating agent, e. g., dimethyl sulfate, methyl iodide, isopropyl iodide, etc. Preferably a basic catalyst, e. g., potassium carbonate, caustic soda, sodium ethylate, silver oxide, or the like, is employed.

Example 1

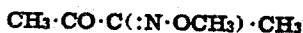
Preparation of the methyl ether of α iso-nitroso methyl propyl ketone:



Heated in a sealed tube for about 15 hours at $100^\circ C$., 3 grams of iso-nitroso methyl propyl ketone dissolved in 26.5 cc. of $N-NaOH$ and 5 g. of freshly distilled CH_3I react to produce the ether oxime. The ether oxime extracted with ether and finally dried with K_2CO_3 may be distilled under reduced pressure at about $50^\circ C$. (25 to 32 mm. mercury absolute) giving a yield of about 40 to 50% theoretical.

Example 2

Preparation of the methyl ether of iso-nitroso methyl acetone (methyl ether or nitrone of diacetyl monoxime).



One mole of iso-nitroso methyl acetone (iso-nitroso methyl ethyl ketone) in an excess of 10% $NaOH$ and shaken for about $\frac{1}{4}$ to $\frac{1}{2}$ hours with dimethyl sulfate at about $45^\circ C$. An oily liquid resulting as the dimethyl sulfate disappears, is extracted with ether and dried.

Comparisons of ignition accelerating action demonstrate definitely that the ester and ether oximes have more than twice the potency of the best oximes or nitroparaffins.

Tests were made on a number of samples prepared by dissolving from less than 1% to about 3% by volume of each compound to be evaluated in a portion of a 40 cetane number gas oil, the tests being made with a high speed C. F. R. Diesel engine according to the method disclosed in the S. A. E. Journal of June, 1936, page 225. Each sample was given a cetane number rating which was determined by the percentage of normal cetane in a blend consisting of normal cetane and alpha-methyl naphthalene giving comparable performance in the test engine. Since the ignition lag of a blend consisting of normal cetane and alpha-methyl naphthalene is shortened very nearly in proportion to the increase in percentage of cetane by volume, the ignition quality improvement of a hydrocarbon fuel by an addition compound can be determined in terms of the cetane number increase imparted to the fuel by the addition compound.

Among the oximes tested were acetone oxime, butyraldoxime, N-heptaldoxime, cyclohexanone oxime, iso-nitroso acetophenone, and acetyl monomethoxime. Most of these oximino compounds form saturated solutions with the Diesel fuel in concentrations of less than 1%. This is particularly true of the cyclic oximes and acetyl monomethoxime. In no instance, did the oximes confer upon the fuel an increase in cetane number greater than about +1 or +2. In almost all instances the cetane rating change was null or negative. In contrast thereto, their corresponding esters and ethers are more soluble in hydrocarbon fuels, to the extent of 3% and higher, and for concentrations of about 1% increase the cetane number of the fuel by at least +4 and more, making these compounds of practical significance.

It will be appreciated that the present invention is not restricted to any particular type of alkylated oxime because any compound containing an oximino group ($:N-OH$) is subject to the same type of alteration by etherification or esterification.

Every type of oil suitable as a fuel for Diesel engines may be improved by the alkylated oximes added thereto in amounts from a fraction of 1% to the limit of the solubility, preferably from about .5% to 5%. In most general use a hydrocarbon oil boiling above the boiling range of gasoline or kerosene, such as the gas oil fraction used in the tests, would constitute the major proportion of the fuel because a compression-ignition engine operates more satisfactorily with liquid fuel injection. For proper functioning of liquid fuel injection systems, the fuel should have a viscosity of about 30 to 65 Saybolt seconds at $110^\circ F$. Ordinarily a petroleum distillate boiling in the range of 375° to $700^\circ F$. has the desired physical characteristics of a Diesel fuel.

The specific advantages of this invention over the prior art result from the decreased vapor pressure, greater oil solubility, stability, ignition accelerating potency, and reduced acidity imparted to oximo compounds by etherification or esterification of the oximino function.

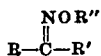
Small quantities of these improved addition agents may be used for improving crude high boiling distillate or residual oils of any base stock, whether it be paraffinic or naphthenic, and with bituminous destructive distillation products or extracts. They may be used with other addition agents for improving other qualities of the oil or together with other ignition quality promoters, e. g., nitrates. It is evident that the modified

oximino compound may also contain other functional groups which make organic compounds more sensitive to ignition, for example nitrate groups or known sulfur groups. Also sulfur analogues of the ether or ester oximes may be used.

The foregoing description and examples are to be taken as illustrative only and not as limiting the scope of the invention. Any modification or variation therefrom conforming to the spirit of the invention is intended to be included within the scope of the claims.

We claim:

1. A composition of matter comprising a hydrocarbon oil having a higher boiling range and viscosity than kerosene blended with a minor proportion of a compound having the type formula:



where R, R' and R'' are aliphatic radicals.

2. A compression-ignition engine fuel comprising

ing a hydrocarbon Diesel fuel blended with a minor quantity of an ether oxime in sufficient amount to improve the ignition quality of the fuel.

3. A compression-ignition engine fuel comprising a hydrocarbon Diesel fuel blended with a minor quantity of an alkyl ether derivative of an oximino compound.

4. A compression-ignition engine fuel comprising a hydrocarbon Diesel fuel and a minor quantity of alkyl ether of an iso-nitroso ketone.

5. A compression-ignition engine fuel comprising a hydrocarbon Diesel fuel blended with methyl ether of iso-nitroso methyl acetone.

6. A compression-ignition engine fuel comprising a hydrocarbon Diesel fuel blended with an alkyl ether of a ketoxime.

7. A compression-ignition engine fuel comprising a hydrocarbon Diesel fuel blended with an alkyl ether of an aldoxime.

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