

# UNITED STATES PATENT OFFICE

2,268,384

## IGNITION PROMOTER FOR DIESEL FUELS

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velopment Company, a corporation of Delaware

No Drawing. Original application July 21, 1938,  
Serial No. 220,500. Divided and this applica-  
tion January 29, 1941, Serial No. 376,472

9 Claims. (Cl. 44-9)

This invention has as its chief object the im-  
provement of fuels for use in compression-ignition  
engines and relates particularly to the use of  
novel addition agents for improving the ignition  
qualities of hydrocarbon fuels when they undergo  
combustion in such engines of the high speed  
Diesel type.

In consideration of increasing the power and  
fuel economy in the operation of compression-  
ignition engines, principally when the hydrocar-  
bon fuel contains insufficient amounts of hydro-  
carbon compounds recognizable as serving these  
ends by virtue of their suitable ignition qualities,  
the additions of various oxygen-, nitrogen-, and  
sulfur-containing organic compounds have been  
proposed. Hydrocarbon compounds characterized  
by aromatic hydrocarbons have poor ignition  
qualities which give rise to the vibrations mani-  
fested by "knocking" and result in a loss of power.  
A poor ignition quality in a fuel is most frequently  
exhibited by an excessive ignition lag, in other  
words, an excessive delay between the beginning  
of fuel injection into the combustion chamber of  
an engine and the point at which ignition of the  
injected fuel sets in.

On the other hand, normal aliphatic hydrocar-  
bons have good ignition qualities. Normal  
cetane, in particular, which serves as a standard  
of high ignition quality in Diesel fuel rating by  
recommendation of the S. A. E. Volunteer Group  
for Compression-Ignition Fuel Research, has a  
very short ignition lag. The ignition lag of a fuel  
consisting of cetane and alphamethyl-naphthalene  
is shortened very nearly in proportion to the  
increase in the percentage of cetane by volume in  
such a blend, and when small amounts of addi-  
tion agents improve the performance of a fuel in  
the same respect comparable to the improvement  
made by an increase of about 5% or more of  
cetane in a blend with alphamethyl-naphthalene,  
such addition agents have been considered as  
having commercial significance.

The novel addition agents of this invention are  
characterized by organic compounds containing a  
thiocarboxylic acid radical, particularly a dithio-  
carboxylic acid or thiolic acid radical, and those  
also containing nitrogen. The solution in liquid  
hydrocarbon fuels of this type of compounds in  
small amounts for imparting better ignition quali-  
ties to the fuels constitutes a more specific object  
of this invention.

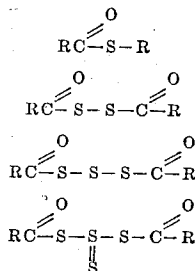
This is a divisional application of our copend-  
ing application, Serial No. 220,500, filed July 21,  
1938. In this divisional application is particu-  
larly claimed the improvement of Diesel fuels by

the ignition promoting compounds characterized  
by containing both a thiocarboxylic acid radical  
and a nitrogen constituent, as exemplified by  
thiocarbamates and thiurams.

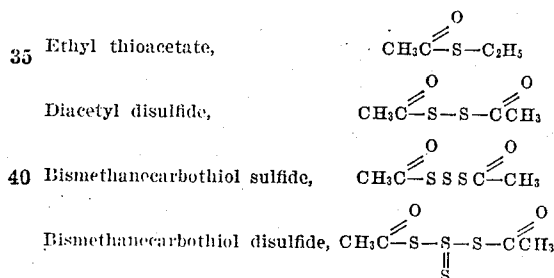
5 Classes of compounds which characteristically  
contain thiocarboxylic acid radicals are: acyl  
sulfides, xanthates, xanthogenyl sulfides, thio-  
xanthogenyl sulfides, thiocarbamates, and thi-  
urams.

10 To these classes of compounds, have been  
assigned some of the following structural formu-  
lae in which R represents generally organic  
groups containing hydrogen and carbon, but prefer-  
ably an alkyl group such as ethyl, propyl, and  
15 higher homologous groups, their isomers, and  
olefinic analogues.

### I. MONOTHIOCARBOXYLIC ACID OR THIOLIC ACID DERIVATIVES, I. E., ACYL SULFIDES

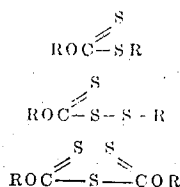


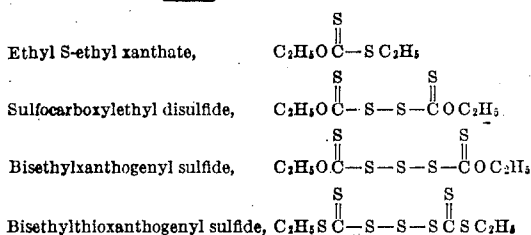
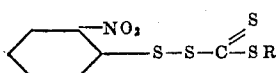
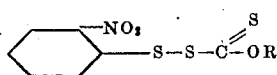
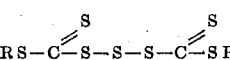
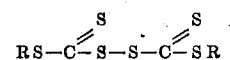
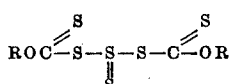
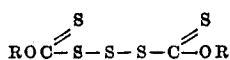
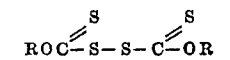
for example:



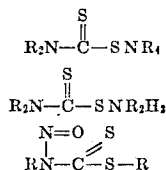
### II. DITHIOCARBOXYLIC ACID DERIVATIVES

a) Xanthogenyl and thioxanthogenyl compounds

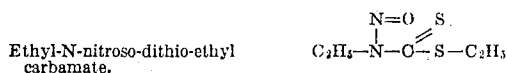
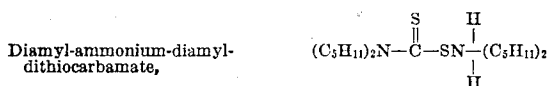
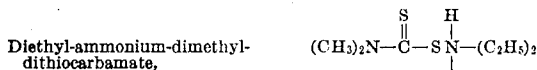




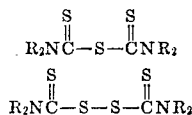
(b) *Dithiocarbamates*



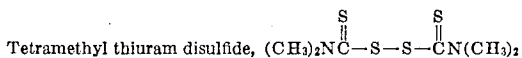
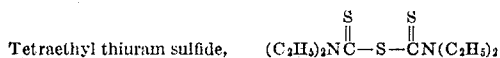
for example:



(c) *Thiurams*

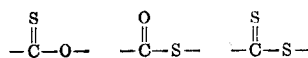


for example:



It is readily apparent that a common characteristic of all the foregoing active compounds is the thiocarboxylic acid group, and particularly such a group with one or more sulfur atoms attached to a carbon atom which has a double bond linkage to sulfur or oxygen as in dithiocarboxylic acid, thiolic acid, or their derivatives. Accordingly, the monothio- and dithio-carboxyl-

ic radicals which may be depicted as occurring in the three configurations:



are considered essential active parts of the compounds which are suitable for the purposes of the present invention, and preferably the compounds should contain only 2 to 3 sulfur atoms in a straight chain linkage, except when sulfur is interlinked between carbon and nitrogen as in the thiocarbamates.

The effectiveness of compounds containing an active thiocarboxylic acid radical in raising the cetane number of a hydrocarbon fuel is illustrated by the following tabulated results from comparative tests on a sample of an unmodified fuel oil and on samples of the same fuel oil modified by small amounts of these compounds.

*Fuel tests*

Compound blended with a 40 cetane Columbian gas oil	Percent of compound in fuel	Cetane number increase
Bismethanecarbothiol sulfide	1.0	+5
Bismethanecarbothiol disulfide	1.0	+9
Bisamylthioxanthogenyl sulfide	3.0	+6
Sulfocarboxylethyl disulfide	3.0	+8
Bisethylxanthogenyl sulfide	3.0	+15
Dimethyl ammonium dimethyl dithiocarbamate	<3.0	+5
Diethyl ammonium diethyl dithiocarbamate	1.0	+10
Tetramethyl thiuram disulfide	1.0	+6
Sodium N-dibutyl dithiocarbamate	<3.0	+6

The proportion of the ignition quality improving agent to be added to the hydrocarbon fuel may range from a fraction of one percent to the limit of solubility in the fuel, but preferably from about .025 to 5%. A gas oil boiling from about 400° F. to 700° F., or 750° F., or, in general, having a suitable boiling range for use as a fuel in Diesel type engines may be used as the hydrocarbon fuel. Under some circumstances, a more narrowly cut fraction such as one distilling from about 400° F. to 600° F. or from 500° F. to 700° F. may be used. Ordinarily, the hydrocarbon fuel may be said to have a boiling range above that of gasoline.

This invention makes commercially feasible the preparation of Diesel fuels giving satisfactory engine performance from crude oils, gas oils, and residual fuels having low pour points, low A. P. I. gravities, and high heat values, such as those procured from naphthene base, asphalt base, mixed base stocks by the addition of active compounds, described, in small quantities. The burning qualities of gas oils from paraffin crudes are also enhanced by these novel addition agents.

Small quantities of the novel addition agents of this invention may be used for adapting various mixtures of hydrocarbons for use as Diesel fuels, including recycle stock from a cracking operation, non-paraffinic extracts, oils from destructive distillations of pyrobituminous and asphaltic materials, mixtures of these with one another or with crude petroleum fractions. Other agents for enhancing various other qualities without detracting substantially from the ignition qualities of the fuel may be admixed, such as, oiliness agents, sludge dispersers, dyes, corrosion inhibitors, anti-oxidants, viscosity improvers, pour-depressants, and gum solvents. Also, other promoters of ignition qualities may be admixed.

It is not intended that this invention be limited to the specific examples which are given merely for the sake of illustration. It is desired to claim all the novelty inherent in the invention in the appended claims as broadly as the prior art permits. 5

We claim:

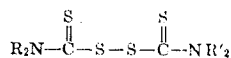
1. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of about 1% to about 5% of an organic compound containing an active thiocarboxylic acid radical and nitrogen for imparting better ignition qualities to the fuel. 10

2. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of about 1% to about 5% of an organic compound containing an active dithiocarboxylic acid radical with sulfur interlinked between carbon and nitrogen for imparting better ignition qualities to the fuel. 15

3. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of about 1% to about 5% of a dithiocarbamate for imparting better ignition qualities to the fuel. 20

4. A fuel for compression-ignition engines of the Diesel type, comprising essentially a hydrocarbon fuel and a small amount of about 1% to about 5% of diethyl ammonium diethyl dithiocarbamate for imparting better ignition qualities to the fuel. 30

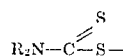
5. An improved Diesel fuel oil containing, in sufficient amount to decrease the ignition delay period of the oil, a compound having the formula:



wherein R and R' are hydrocarbon radicals.

6. An improved Diesel fuel oil containing tetramethyl thiuram disulfide in sufficient amount to decrease the ignition delay period of the fuel.

7. The method of accelerating ignition of a hydrocarbon Diesel fuel in a Diesel type compression-ignition engine, which comprises admixing with the fuel prior to its ignition in the engine a minor proportion of about 1% to about 5% of a compound containing a thiocarboxylic radical and nitrogen in the group:



wherein R<sub>2</sub> represents hydrocarbon radicals, to impart better ignition qualities to the fuel.

8. The method described in claim 7, in which said compound containing a thiocarboxylic radical and nitrogen is a dithiocarbamate. 25

9. The method described in claim 7 in which said compound containing a thiocarboxylic radical and nitrogen is a thiuram sulfide.

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