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2,934,048

COMPOSITION

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My invention relates to a starting fluid for use in compression ignition engines which is particularly valuable in cold weather for low temperature starting. In particular, my invention provides fluids effective at sub-zero temperatures down to about -40° F.

It is well known that compression ignition engines employing regular diesel fuels are difficult to start under conditions of low ambient temperature particularly at temperatures below about 32° F. In starting a cold engine, the temperature within the cylinder must be sufficiently high to ignite the regular fuel. Such temperatures are developed only after sufficient work has been done in compression of the charges within the working cylinder to bring the parts of the engine in direct heat exchange relation with the contents of the working cylinder, as well as the charge undergoing compression, to a relatively high temperature. Thus, at low ambient temperatures it is often difficult, if not impossible, to attain such required temperatures without special equipment and starting methods.

With the widespread use of diesel engines, particularly in mobile auto-powered equipment in the transportation, construction and military fields, cold weather starting difficulties for such engines often involve serious economic loss above the mere delay in use of the automotive equipment. Delay of starting is, of course, extremely important in military equipment. Hence considerable time and attention have been given to the problem of obtaining reliable and inexpensive positive cold weather starting methods. Such methods employ winterizing techniques and mechanical starting aids, for example, combustion type air induction heaters, glow plugs, external heaters for engine jacket coolants, jacketed crankcases, jacketed battery cases and the like.

One such method for starting of compression ignition engines contemplates the use of an auxiliary fuel, a starting fluid, in combination with the regular, primary fuel. The auxiliary fluid, for example diethyl ether, is finely aspirated by suitable means into the air intake system of the engine during starting until combustion of the regular injected fuel is continuous.

I have discovered that volatile organic nitrates, particularly alkyl nitrates, e.g. amyl nitrate, possess specially desirable properties, such as marked ignition response to low temperatures and pressures, when atomized into the intake air of a diesel engine, which properties render them useful aids in cold weather starting of diesels. I have also discovered that blends of an alkyl nitrate, a 4 carbon atom alkyl ether and a predominantly straight chain paraffinic, low pour point, light, close cut petroleum fraction boiling within the approximate range of 200° to 350° F. consisting essentially of C_7 , C_8 , C_9 or C_{10} normal-paraffin cuts or mixtures thereof, e.g., normal-heptane, possess additional extremely useful properties highly desirable in diesel starter fluids. My invention

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provides a starting fluid containing about 10 to 70 percent by volume of the ether, about 10 to 70 percent by volume of the alkyl nitrate and about 10 to 60 percent by volume of the light paraffinic fraction. Compositions of maximum performance effectiveness fall within the approximate range of about 20 to 50 percent by volume of the ether, about 20 to 50 percent by volume of alkyl nitrate and about 20 to 50 percent by volume of the light paraffinic fraction. I prefer a composition of about 40 percent by volume of diethyl ether, about 20 percent by volume of amyl nitrate and about 40 percent by volume of normal-heptane. I particularly prefer a composition of about 40 percent by volume of diethyl ether, about 40 percent by volume of amyl nitrate and about 20 percent by volume of normal-heptane.

The starting fluids of my invention provide effective cold starting fluids suitable for sub-zero use when properly applied to the intake manifold of an internal combustion engine. In particular, the fluids are effective at all fluid temperatures down to about -40° F. as compared with only -27° F. for diethyl ether alone. Also, burning of the fluid is smooth and detonation is reduced significantly. Diethyl ether alone produces disadvantageous severe detonation. Diethyl ether burns so rapidly when ignited that severe detonation may be produced due to extremely high rate of pressure rise. Due to the rapid rate of heat release, diethyl ether may fail to ignite the regular diesel fuel simultaneously injected.

The fluids possess a valuable combination of properties which provides a fluid of significantly improved performance characteristics. For example, the fluids have an equivalent cetane number in excess of 100 and thus have a correspondingly short ignition delay. They possess a spontaneous ignition temperature of slightly below 380° F. and are highly pressure and temperature sensitive to ignition. Such fluids, therefore, ignite quickly at the low compression pressures and temperatures which prevail at low engine cranking speeds at sub-zero temperatures. The pronounced pre-flame reaction characteristics exhibited by fluids of this type plus their low rate of pressure rise after ignition results in a significant reduction in detonation. The longer burning duration of fluids of this type due to nature of the constituents results in earlier ignition of the regularly injected diesel fuel, thus engine warm-up time is reduced. These properties coupled with volatility characteristics suitable for achieving a high degree of atomization where properly applied at low temperatures result in a highly effective type of fluid starting aid. While the blends are sufficiently volatile for aspiration into the engine intake air by suitable means to give a finely comminuted fluid/air mixture capable of being drawn into the combustion chambers without drop-out of the fluid particles en route under severely cold weather conditions, yet such volatilities are insufficient to amount to a hazardous problem in warm weather and consequently the blended fluids can be conveniently stored and handled. These properties are highly desirable for effective starting fluids.

The useful predominantly paraffinic, low pour point, light petroleum fractions are those composed mainly of one or more of the normal paraffins heptane, octane, nonane and decane. Representative constituents of gasolines such as aromatics, naphthenes, olefins, iso-paraffins, and the lower boiling point n-paraffins are unsuitable as cold starting aids. Higher boiling point n-paraffins are unsuitable due to their high freezing points. Preferably, the paraffinic petroleum fraction is normal-heptane. The n-heptane can contain minor amounts of other materials such as isomers or close homologues but

these materials preferably should not exceed about 15 percent. Preferably, the n-heptane is 99 percent pure.

The alkyl nitrates useful in my invention are primary and secondary alkyl nitrates containing from 4 to 8 carbon atoms, for example, butyl, amyl, hexyl, heptyl and octyl nitrates. Preferably, amyl nitrate is used. The amyl nitrate can be normal-amyl or iso-amyl or other isomers, for example, 2-methyl-1-butyl nitrate. The 4 carbon atom ethers which I employ include diethyl ether, methyl propyl ether and methyl isopropyl ether. The fluids of my invention or the primary fuel with which they are used, e.g., diesel fuel, can contain other components.

In evaluating the effectiveness of various materials possessing potential merit as starting fluids a useful tool can be employed. This tool is a variable compression ratio, single cylinder, turbulent chamber CFR engine. It is well known that the critical compression ratio (CCR) of a diesel fuel is a reliable measure of ease of ignition (ignition delay period). The lower the compression ratio at which auto-ignition takes place under a given set of test and engine operating conditions the better the fuel from the standpoint of ease of ignition. If the critical compression ratio of a given diesel fuel employed for reference is first established and then a potentially effective starting fluid introduced into the intake air of the engine, simultaneously with injection of the reference diesel fuel and under prescribed conditions, a critical compression ratio lower than that obtained with the reference diesel fuel should be obtained if the material being evaluated as a starting fluid possesses any merit. Thus the magnitude of difference between the two critical compression ratios, termed the critical compression ratio difference (CCRD), provides a yard stick for measuring the effectiveness of such materials. The greater the CCRD the greater the effectiveness of the starting fluid. CCRD data have been previously correlated with actual cold weather experiments and have been demonstrated to provide accurate relative prediction of cold weather starting when obtained on a motored test engine at reduced cooling jacket temperatures and at a speed of 900 r.p.m. For exploratory evaluations, data obtained by the CCRD method are to be preferred to actual cold starting data obtained on full scale engines due to speed of measurement, closer control of test variables and test economies. Where herein referred to, the CCRD data were derived under the following conditions using a single cylinder CFR diesel with a turbulent combustion chamber.

Coolant temperature..... 10° F.
Primary fuel injection rate..... 13 cc. per minute.

To evaluate the starting characteristics and effectiveness of secondary fuel aspirated with the air intake, the further test conditions were employed:

Primary fuel used..... 50 cetane number diesel fuel of 350-675° F. boiling range.

Quantity secondary fuel aspirated
per trial..... 7 cc. in 10 seconds.

The engine was constantly motored at 900 r.p.m. under equilibrium conditions except for 10-second fuel injection at each trial. The initial compression ratio for the engine was set below the point at which ignition of the primary fuel occurred for an injection duration of 10 seconds. From this point the compression ratio was gradually raised at 10-second intervals until the critical compression ratio of the primary fuel was reached, as evidenced by continuous combustion of the fuel. When this value was determined by three separate determinations, the compression ratio was again substantially lowered and the critical ratio of the primary fuel plus aspirated secondary fuel was determined in like manner.

The difference between the two values represents the critical compression ratio difference (CCRD) of the secondary fuel.

Under these test conditions the CCRD data were determined using as starting fluids diethyl ether, a proven and well known auxiliary starting fluid; amyl nitrate; normal-heptane; blends of diethyl ether and normal-heptane (a starting fluid described in my U.S. Patent 2,575,543 issued November 20, 1951); and blends of diethyl ether, amyl nitrate and normal-heptane in various proportions by volume. The following table illustrates the results:

Table I

Fluid:	CCRD value
15 Diethyl ether.....	6.07
Amyl nitrate.....	4.11
Normal heptane.....	1.13
20 20% diethyl ether+80% n-heptane.....	4.74
40% diethyl ether+60% n-heptane.....	5.24
60% diethyl ether+40% n-heptane.....	5.54
20% diethyl ether+20% amyl nitrate+60% n-heptane.....	5.64
20% diethyl ether+40% amyl nitrate+40% n-heptane.....	5.87
25 20% diethyl ether+60% amyl nitrate+20% n-heptane.....	6.29
40% diethyl ether+20% amyl nitrate+40% n-heptane.....	6.32
60% diethyl ether+20% amyl nitrate+20% n-heptane.....	6.53
30 40% diethyl ether+40% amyl nitrate+20% n-heptane.....	6.54

As illustrated by the above data, surprisingly, blends of diethyl ether, amyl nitrate and normal-heptane exhibited better performance characteristics for cold weather starting as measured by the CCRD value, than are exhibited by either diethyl ether, amyl nitrate or normal-heptane alone or by blends of diethyl ether and normal-heptane. It is particularly surprising that the blends of our invention provide better performance characteristics than diethyl ether since diethyl ether is one of the most effective of starting fluids previously known. This is believed to be due to the effects of the various desirable qualities of our starting fluid, namely, rapid triggering of ignition of the fluid, low rate of pressure rise after ignition, extended burning of the fluid over a fairly wide range of engine crank angles and volatility suitable for the formation of finely comminuted mixtures with air when atomized into the intake air by suitable means. It is to be noted that as the three component blends contain amounts of normal-heptane approaching the useful upper limit of 60%, the CCRD value approaches that of the two component blends containing similar amounts of heptane.

Moreover the above results show that amyl nitrate is almost as effective a secondary fuel as diethyl ether, as it has a CCRD value approaching that for diethyl ether. However, amyl nitrate is not as useful in extremely cold weather since it has low volatility. The blends of amyl nitrate, diethyl ether and normal-heptane, however, surmount these difficulties, having the requisite low pour point characteristics and volatility for atomization with the air intake even under severely low temperatures.

Other tests were performed to determine the time required for starting engines using a blend of 40% amyl nitrate, 40% diethyl ether and 20% n-heptane as a starting fluid. The engines were full scale automotive diesel engines. The tests were run in a laboratory "cold room." The engines, batteries and starting fluid were cold soaked at the test temperature for a period of 24 hours prior to making a starting trial. The primary fuel used corresponded to winter grade diesel fuel, DF-1 as specified

under Federal specification VV-F-800, December 17, 1954. Its characteristics were as follows:

Flash point, P.M., ° F.....	110
Cloud point, ° F.....	-58
Pour point, ° F.....	-80
Kinematic viscosity at 100° F., centistokes.....	1.260
Water and sediment, percent vol.....	Trace
Sulfur, percent.....	0.084
Carbon residue 10% res., percent.....	0.080
Ash, percent.....	0.0
Copper strip corrosion at 212° F.....	0
Cetane number.....	47.5
Distillation, ° F.:	
IBP.....	306
10.....	333
50.....	369
90.....	499
EP.....	549
Gravity, ° API.....	46.3

The lubricating oil corresponded to MIL-O-10295. The starting fluid was injected into an intake manifold at the point of maximum air flow velocity. The time required to fire and sustain combustion until the engine can operate on regular diesel fuel was measured and is listed under second to start in Table II below. The engines failed to start at the temperatures listed in Table II when no starting fluid was used.

Table II

ENGINE: GM3-71, 3 CYLINDER

Run	Min. Temp., ° F.	Cranking Speed, r.p.m.	Fluid Used, cc. to Start and Run	Seconds to Start and Run
1.....	-26	120	100	61
2.....	-26	115	115	66

ENGINE: BUDA, MODEL 1BD38, SINGLE CYLINDER

1.....	-26	310	6	6
2.....	-26	310	7	5
3.....	-35	330	20	20

ENGINE: 1HC, MODEL UD-14A, 4 CYLINDER

1.....	-23	110	170	45
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The above results show the effectiveness of the starting fluid in starting diesel engines at sub-zero temperatures.

The manner in which starting fluids are best used is known to the art. For details and different suggested methods of aspiration I make reference to my U.S. Letters Patent No. 2,575,543, issued November 20, 1951.

I claim:

1. A starting fluid for compression ignition engines consisting essentially of about 10 to 70 percent by volume of an alkyl ether of 4 carbon atoms, about 10 to 70 percent by volume of an alkyl nitrate of from 4 to 8 carbon atoms, and about 10 to 60 percent by volume of a predominantly straight chain paraffinic, low pour point, light close cut petroleum fraction boiling within the approximate range of 200 to 350° F. and containing from 7 to 10 carbon atoms.

2. The fluid of claim 1 in which the alkyl nitrate is amyl nitrate, the alkyl ether is diethyl ether and the paraffinic petroleum fraction is normal-heptane.

3. The fluid of claim 1 in which the percent of alkyl ether is 20 to 50, the percent of alkyl nitrate is 20 to 50, and the percent of paraffinic petroleum fraction is 20 to 50.

4. The fluid of claim 3 in which the alkyl nitrate is amyl nitrate, the alkyl ether is diethyl ether and the paraffinic petroleum fraction is normal-heptane.

5. A starting fluid for compression ignition engines consisting essentially of about 40 percent by volume of diethyl ether, about 20 percent by volume of amyl nitrate and about 40 percent by volume of normal-heptane.

6. In the operation of internal combustion engines of the compression ignition type, the improvement which comprises burning a primary fuel while introducing with the air supply the fluid of claim 1.

7. In the operation of internal combustion engines of the compression ignition type, the improvement which comprises burning a primary fuel while introducing with the air supply the fluid of claim 2.

8. In the operation of internal combustion engines of the compression ignition type, the improvement which comprises burning a primary fuel while introducing with the air supply the fluid of claim 3.

9. In the operation of internal combustion engines of the compression ignition type, the improvement which comprises burning a primary fuel while introducing with the air supply the fluid of claim 4.

10. In the operation of internal combustion engines of the compression ignition type, the improvement which comprises burning a primary fuel while introducing with the air supply the fluid of claim 5.

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