

LUBRICATING OIL FOR
A DIESEL POWERED ENGINE AND METHOD OF OPERATING A DIESEL
POWERED ENGINE

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This invention relates to the reduction of NO_x emissions from a diesel powered engine and lubricating oil compositions useful for such diesel-powered engine.

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Diesel engine manufacturers are continuously challenged to meet lower emission standards set forth by the U.S.

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Environmental Protection Agency (EPA), as well as other such agencies worldwide. These standards for both diesel and gasoline engines mandate limits for unburned hydrocarbons, carbon monoxide and nitrogen oxides (NO_x). Current U.S. regulations for diesel engine emissions allow NO_x emissions of only 4.0 g/bhp-hr. This will be reduced for the 2004 Model Year to a standard of 2.5 g/bhp-hr combined NO_x and non-methane hydrocarbons emissions.

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The undesirability of NO_x compounds and their ability to further react to produce additional undesirable materials make them an undesirable by-product from the burning of hydrocarbons. These NO_x compounds and their derivative reaction products comprise what is commonly referred to as

30

"smog."

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Many methods have been used or suggested to reduce or eliminate NO_x. A number of these rely upon reaction of NO_x in the effluent exhaust gas in a system containing a reducing agent. Reducing agents such as ammonia, urea, and cyanuric acid have been used to selectively reduce NO_x (NO + NO₂) in the exhaust gas streams.

The NO_x reduction steps in a effluent exhaust gas system can take place at low temperature over a catalyst, referred to as selective catalytic reduction (SCR), or at high

5 temperature without the aid of a catalyst (selective non-catalytic reduction, or SNCR).

A recent example of SCR can be found in U.S. 6,203,770 B1. This patent describes the pyrolysis of urea ($\text{CO}(\text{NH}_2)_2$) in a chamber generating ammonia (NH_3) and isocyanic acid (HNCO).
10 These components are then mixed with NO_x containing exhaust gases from a diesel engine and contacted with an SCR catalyst resulting in the reduction of NO_x compounds.

Some in-cylinder technologies for reducing NO_x have also been developed, such as exhaust gas recirculation. One way
15 of implementing this method involves recirculating a portion of the exhaust gases back through the engine using pressure pulses created by the exhaust valves. The exhaust gases go through a cooler before being introduced back into the engine through the inlet. These gases dilute the air/fuel charge
20 thereby lowering peak combustion temperatures and lowering NO_x emissions.

All of these technologies require the design and implementation of additional systems for the exhaust gas, which increases costs and complexity, while often reducing
25 engine efficiency.

Another limitation, that involves the SNCR method, is the requirement of a very high temperature, much higher than typical diesel exhaust gas temperatures.

It would be very advantageous to find a method of
30 reducing problematic NO_x emissions from a diesel engine that would not require expensive modifications to the exhaust system of diesel engines.

A lubricating oil composition useful for diesel engine is provided comprising: a base oil; and
35 at least one oil-dispersible source of HNCO in an amount effective to reduce NO_x emission from a diesel engine compared to a lubricating oil composition without the source of HNCO .

5 Also provided is a lubricating oil composition useful
for diesel engine comprising: a base oil; and
at least one isocyanate having sufficient volatility to degas
from the lubricating oil composition under normal engine
operating conditions in an amount effective to reduce NOx
10 emission from a diesel engine compared to a lubricating oil
composition without the isocyanate.

 Further provided is a method of operating a diesel
engine comprising:
introducing into the diesel engine a lubricating oil
15 composition; and
operating the engine,
wherein the lubricating oil composition comprises a base oil,
and at least one oil-dispersible source of HNCO in an amount
effective to reduce NOx emission from a diesel engine
20 compared to a lubricating oil composition without the source
of HNCO.

 Yet further provided is a method of operating a diesel
engine comprising: an engine body; a combustion chamber
formed in the engine body for containing a mixture of fuel
25 and air; a plurality of cylinders formed in the engine body;
and a respective piston mounted in each of said plurality of
cylinders for reciprocal movement through successive exhaust
and intake strokes, each respective piston defining a
combustion chamber for containing a mixture of fuel and air
30 the method comprising:
introducing, into the combustion chamber, diesel fuel and
air;
delivering a lubricating oil composition to the cylinders;
compressing the diesel fuel in the combustion chamber to
35 ignition with the piston thereby generating an exhaust gas
containing NOx;
wherein the lubricating oil composition comprises a base oil
and at least one oil-dispersible source of HNCO.

5 **Fig. 1** is a plot of NO_x emissions versus time for comparative oil and one within the scope of this invention.

Fig. 2 is a graph of NO_x emissions averaged over several experimental runs for comparative oil and also for an oil within the scope of the invention at two different treatment
10 levels.

Fig. 3 is a plot of NO_x emissions for engine tests at 30 and 55 mph steady state speeds for reference oil and oil within the scope of the invention.

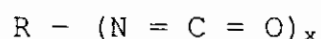
Fig. 4 is a plot of NO_x emissions for engine tests at
15 various speeds for reference oil and oil within the scope of the invention.

 The invention reduces exhaust NO_x emissions in a diesel fuel engine. One aspect of the invention relates to the reduction of NO_x from the exhaust of diesel fuel engines via a
20 NO_x reducing agent introduced via the lubricating oil. The term "diesel fuel engine" or "diesel engine" includes all compression-ignition engines, for both mobile purposes (including marine) and stationary purposes (such as power plants) and of the two-stroke per cycle, four-stroke per
25 cycle and rotary types. The term "diesel fuel" means "distillate fuels" including diesel fuels meeting the ASTM definition for diesel fuels or other fuels even though they are not wholly comprised of distillates and can comprise alcohols, ethers, organo-nitro compounds and the like (e.g.,
30 methanol, ethanol, diethyl ether, methyl ether, nitro methane). The term "distillate fuel" means all of those products prepared by the distillation of petroleum or petroleum fractions and residues. The term "petroleum" is meant in its usual sense to include all of those materials
35 regardless of source normally included within the meaning of the term, including hydrocarbon materials, regardless of viscosity, that are recovered from fossil fuels. The term

5 "diesel oil" is meant to include any motor oil or lubricating oil suitable for use in a diesel engine.

According to the invention, a novel method is disclosed which reduces NO_x emissions from a diesel fuel engine. The method involves adding a novel diesel oil composition to the
10 diesel engine, and then running the engine under normal operating conditions. It has been found that introduction of NO_x reduction species directly into the combustion chamber, would allow reaction of NO_x and reducing species in the presence of sufficiently high temperatures.

15 Accordingly, a lubricating oil composition useful for diesel engine is provided containing: a base oil; and at least one source of HNCO in an amount effective to reduce NO_x emission from a diesel engine compared to a lubricating oil without the source of HNCO. The source of HNCO is
20 preferably dispersible in the lubricating oil composition. The term "dispersible" means that the source of HNCO can be distributed throughout the lubricating oil matrix whether it is soluble, colloidal or suspended. The source of HNCO preferably is an isocyanate having sufficient volatility to
25 degas from the lubricating oil composition under normal engine operating conditions. The term "sufficient volatility to degas" can be the isocyanate in its original form or at least one of its decomposition components. Decomposition components can be the isocyanate, or the source of HNCO,
30 where at least a portion is cleaved to release the cyanogen functionality (NC) under normal operating conditions found in the combustion chamber of the engine. Examples of preferable isocyanates include compounds represented by the formula:



35 wherein R represents a hydrocarbyl group having 4 to 30 carbon atoms, hydrocarbyl group being preferably alkyl, aryl, or arylalkyl group, and x is an integer of 1 to 4, more

5 preferably 1 or 2. Most preferably the isocyanate is methylene diphenyl diisocyanate.

The source of HNCO or isocyanate is present in an amount of at least 0.1% by weight, preferably at least 0.5% by weight, more preferably at least 1.0% by weight based on the
10 total weight of the lubricating oil composition.

Practically, the source of HNCO or isocyanate may be present in an amount where the lubricating oil is effective for its intended purpose as a lubricant that is in an amount of up to 5% by weight based on the lubricating oil composition.

15 Preferably the lubricating oil composition is substantially free of compounds reactive with the HNCO or isocyanates to a level that the source of HNCO or isocyanates is available to reduce the NOx level generated at the engine. The presence of HNCO can be detected by known analytical methods including
20 spectroscopic methods known to those skilled in the art.

The base oil component of this invention may be selected from any of the synthetic (lubricating) oils or natural oils or mixtures thereof. Base oils may be classified as Group I, Group II, Group II+, Group III, and Group IV base oils as
25 known to those skilled in the art. In certain instances, usually depending on the final use of the lubricant composition according to the present invention, Group I is preferred, in some instances Group II+ are preferred, and in other instances, Group II and III are preferred.

30 Typically, group I base oils contain less than 90% saturates (as determined by ASTM D 2007) and/or greater than 0.03 percent sulfur (as determined by ASTM D 2622, D 4294, D 4927, or D 3120) and have a viscosity index greater than or equal to 80 and less than 120 (as determined by ASTM D 2270).
35 Typically group II base oils contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than 80 and less than 120 using the above noted test methods. Group II+ base oils may have a VI

5 at the high end of the VI spectrum, e.g., about 120.
Typically, Group III base oils contain greater than or equal
to 90 percent saturates and less than or equal to 0.03%
sulfur and have a viscosity index greater than or equal to
120 using the tests noted above. Typically group IV base
10 oils are polyalphaolefins (PAO).

The base oils may conveniently have a viscosity of 3.8
Centistokes (mm^2/s) at 100 degree C to 26 Centistokes (mm^2/s)
at 100 degree C.

Natural oils include animal oils and vegetable oils
15 (e.g., castor, lard oil) liquid petroleum oils and
hydrorefined, solvent-treated or acid-treated mineral
lubricating oils of the paraffinic, naphthenic and mixed
paraffinic-naphthenic types. Oils of lubricating viscosity
derived from coal or shale are also useful base oils.

20 Alkylene oxide polymers and interpolymers and
derivatives thereof where the terminal hydroxyl groups have
been modified by esterification, etherification, etc.,
constitute another class of known synthetic lubricating oils.
These are exemplified by polyoxyalkylene polymers prepared by
25 polymerization of ethylene oxide or propylene oxide, the
alkyl and aryl ethers of these polyoxyalkylene polymers
(e.g., methyl-poly isopropylene glycol ether having an
average molecular weight of 1000, diphenyl ether of poly-
ethylene glycol having a molecular weight of 500-1000,
30 diethyl ether of polypropylene glycol having a molecular
weight of 1000-1500); and mono- and polycarboxylic esters
thereof, for example, the acetic acid esters, mixed C_3 - C_8
fatty acid esters and C_{13} Oxo acid diester of tetraethylene
glycol.

35 Another suitable class of synthetic lubricating oils
comprises the esters formed by reacting dicarboxylic acids
(e.g., phthalic acid, succinic acid, alkyl succinic acids and
alkenyl succinic acids, maleic acid, azelaic acid, suberic

5 acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol).

10 Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex

15 ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane,

20 pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as, the polyalkyl-, polyaryl-, polyalkoxy, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricating oils;

25 they include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethyl-hexyl) silicate, tetra-(p-tertbutylphenyl) silicate, hexa-(4-methyl-2-pentoxy) disiloxane, poly(methyl)siloxanes and poly(methylphenyl) siloxanes. Other synthetic lubricating

30 oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

These lubricating oil compositions may typically contain other additives such as oxidation inhibitors (antioxidants),

35 dispersants, and/or detergents. The lubricating oil compositions may also include other lubricant additives that perform specific functions not provided by the main components. These additional additives include, but not

5 limited to, corrosion inhibitors, viscosity index improvers
(or modifiers), pour point depressants, zinc
dialkyldithiophosphates, anti-wear agents, anti-foam agents,
and/or friction modifiers. Suitable additives are described
in U.S. Patent Nos. 5,320,765 and 6,528,461. Suitable
10 oxidation inhibitors include, for example, copper
antioxidants, phenolic compounds, and/or aminic compounds.
Suitable dispersants include, for example, succinimides.
Suitable detergents include, for example, one or more
salicylate, phenate, and/or sulfonate detergents.

15 The diesel engine typically comprise: an engine body; a
combustion chamber formed in the engine body for containing a
mixture of fuel and air; an intake air system for delivering
intake air, including at least one of air and a mixture of
air and fuel, to said combustion chamber; an exhaust gas
20 system for directing exhaust gas that may contain air and the
combustion products of fuel from said combustion chamber; a
fuel supply system connected to the engine for directing fuel
into at least one of said intake air system and said
combustion chamber; a plurality of cylinders formed in the
25 engine body, said cylinders comprising an inner edge; a
respective piston mounted in each of said plurality of
cylinders for reciprocal movement through successive exhaust
and intake strokes, each respective piston defining a
combustion chamber for containing a mixture of fuel and air,
30 said piston having piston rings that provide sliding seal
between the outer edge of the piston and the inner edge of
the cylinder; a respective rotatable crankshaft operatively
connected to said respective piston for reciprocal movement
through a top dead center position as such delivers power to
35 the drive train; and a sump (crankcase) formed in the engine
body for containing a lubricating oil and surrounding the
crankshaft. The cylinders contain an inner wall (or inner
edge) and an outer wall where the inner circumferential wall

5 surrounds the piston. The piston rings typically are present to prevent the fuel/air mixture and exhaust in the combustion chamber from leaking into the sump during compression and combustion and to keep lubricating oil in the sump from leaking into the combustion area. The combustion chamber is
10 where the combustion and compression takes place. As the piston moves up and down the cylinder, the volume of the combustion chamber changes defining the maximum volume and minimum volume of the combustion chamber (expansion and/or compression strokes). The combustion event occurs during the
15 compression and/or expansion strokes.

In the method of the instant invention, a method of operating a diesel engine such as described above comprising an engine body; a combustion chamber formed in the engine body for containing a mixture of fuel and air; a plurality of
20 cylinders formed in the engine body, said cylinders comprising an inner edge; a respective piston mounted in each of said plurality of cylinders for reciprocal movement through successive exhaust and intake strokes, each respective piston defining a combustion chamber for
25 containing a mixture of fuel and air is provided that reduce NOx emission levels from the diesel engine the method comprising:

introducing, into the combustion chamber, diesel fuel and air;
30 delivering a lubricating oil composition to the cylinders; compressing the diesel fuel in the combustion chamber to ignition with the piston thereby producing (generating) an exhaust gas containing NOx;
wherein the lubricating oil composition comprises a base oil
35 and at least one oil-dispersible source of HNCO. The source of HNCO is preferably an isocyanate having sufficient volatility to degas from the lubricating oil composition under normal engine operating conditions. In general,

5 pressures in the range from 500 psi to 1000 psi can be
reached at the end of the compression stroke. Through the
compression process, the air can be heated up to 537 °C (1000
°F) or higher, which is high enough to spontaneously ignite
the fuel as it is injected into the cylinders. Temperatures
10 of the combustion gases following ignition of the fuel are
higher, rising as high as 1600 °C (2912 °F) a few crank-angle
degrees after ignition of the fuel. The cylinder is
typically heated during such engine operating conditions to a
temperature in the range of 300 °F (149°C) to 500 °F (260°C).

15 Without limiting the invention by any certain theory, it
is theorized that a NO_x reducing component degasses from the
oil proximate and/or on the inner edge of the cylinders while
the engine is operating (at the temperature of the
cylinders) and reacts with the combustion gas. It has been
20 found that when the source of HCNO is added to the
lubricating oil, the concentration of NO_x emissions in the
exhaust gases of a diesel engine is reduced compared to
emissions from the same diesel engine operated with a
reference oil without the source of HCNO. The lubricating
25 oil is introduced into the sump or crankcase. The
lubricating oil contained in the bottom of the sump is
generally delivered to the cylinders that may be deposited
proximately and/or on the inner edge of the cylinders by
means of the crankshaft and the piston. The present
30 invention will be illustrated by the following illustrative
embodiment, which is provided for illustration only and is
not to be construed as limiting the claimed invention in any
way.

35 EXAMPLES

Test runs to evaluate lubricating engine oil
compositions for reducing NO_x emissions were performed using
an industry standard diesel powered test engine.

5 **Test Equipment:** A Caterpillar® single cylinder oil test engine (SCOTE) was used to evaluate the diesel engine oil compositions. The SCOTE engine did not have any catalytic converters or any apparatus to lower NO_x emissions. The exhaust system was modified to accommodate a zirconia NO_x sensor, the signal of the sensor was inputted to a portable NO_x meter (e.g., Horiba NO_x meter, Japan).

The evaluation tests were conducted using the following lubricating oil composition and fuel.

15 **Test Oil/Fuel:** A commercially available, fully formulated 15W40 diesel engine oil was used as reference oil. A test lubricating composition was prepared by combining a commercially available, fully formulated, 15W40 diesel engine oil with 0.5 % by weight of an isocyanate, methylene diphenyl diisocyanate(MDI) (Dow Chemical Company, Midland Michigan), based on the weight of the lubricating composition. Fuel for the test runs was an ASTM reference diesel fuel.

The evaluation tests were conducted according to the following procedure.

25 **Test Description:** A modified CAT 1P ASTM test method was performed to generate NO_x emissions. Stages 4 and 5 of the CAT 1P ASTM test method were run for two hours. NO_x emissions were measured during the testing period every 6 minutes. The NO_x emissions data were recorded using the SCOTE test system data logger. All test runs were performed in duplicate and the data were averaged. Results from the evaluation testing are graphically depicted in Figures 1 and 2. Figure 1 is a graphical representation of NO_x emissions versus time for the reference oil and the test lubricating oil composition containing 0.5 wt.% of MDI, based on the weight of the lubricating oil composition. The results as shown in Figure 1 demonstrate that the MDI containing lubricating oil composition significantly reduces NO_x emissions generated by a single cylinder diesel engine. NO_x emissions were reduced to

5 1450 parts per million (ppm) from a level of 1645 ppm for the reference oil.

Subsequent tests were conducted to evaluate the effect of different MDI concentrations on NO_x emissions using the same procedure, engine, fuel and reference oil described for Figure 1. The test lubricating oil compositions for the subsequent testing were prepared by combining commercially available, fully formulated, 15W40 motor oil meeting API standards with at 0.5 wt.% of an isocyanate, MDI, or 1.0 wt.% of an isocyanate, MDI, based on the weight of the lubricating oil composition. Figure 2 shows the average of fifteen runs for the reference oil, 1611 ppm NO_x, the average of five runs for the test lubricating oil composition containing 0.5% by weight MDI, 1486 NO_x, and the average of two runs with the test lubricating oil composition containing 1.0% by weight MDI, 1573 ppm. NO_x emission data for the reference oil is tabulate in Table I. NO_x emission data for the test lubricating oil composition at 0.5% by weight is tabulated in Table II. NO_x emission data for the test lubricating oil composition at 1.0% by weight is tabulated in Table III.

5 Table I - NO_x Emissions When Using Reference Oil

Test Run	NO _x in exhaust (ppmw)
1	1563
2	1645
3	1523
4	1648
5	1576
6	1570
7	1597
8	1696
9	1656
10	1668
11	1559
12	1572
13	1694
14	1545
15	1646
Average	1611

10 Table II - NO_x Emissions When Using Oil Containing 0.5% by Weight of MDI

Test Run	NO _x in exhaust (ppmw)
1	1440
2	1429
3	1482
4	1463
5	1615
Average	1486

5 Table III - NO_x Emissions When Using Oil Containing 1.0% by
Weight of MDI

Test Run	NO _x in exhaust (ppmw)
1	1495
2	1650
Average	1573

10 Further tests were conducted using a commercially
available diesel powered truck engine.

Test Equipment: A 2000 model year Ford F-250, three-quarter
ton pick up truck was used to evaluate the test oils. The
test vehicle is powered by a 7.3L Navistar V-8 diesel engine,
coupled to a four speed automatic transmission. This vehicle
15 meets original equipment manufacturers specifications, and
thus does not utilize catalytic exhaust converters or an
exhaust gas recycling system. The exhaust system was modified
slightly to accommodate a zirconia NO_x sensor, the signal of
which was input to a portable Horiba NO_x meter. A Campbell
20 Scientific data logger was used to record NO_x data.

The tests were conducted using the following test oil
and fuel.

Test Oil/Fuel: A reference oil and a lubricating oil
composition were evaluated in the diesel powered truck
25 engine. Reference oil was a commercially available, fully
formulated 15W40 diesel engine oil. The test lubricating oil
composition was prepared by combining a commercially
available, fully formulated 15W40 diesel engine oil with 0.5%
by weight (5000 ppm) of methylene diphenyl diisocyanate
30 (MDI) based on the weight of the lubricating oil composition
according to the invention. The reference oil was used to
establish a baseline reference for NO_x emissions. The test
lubricating oil composition was evaluated relative to the

5 resultant NOx emission levels obtained with the reference oil. The program test fuel was a low sulfur #2 diesel fuel.

The tests were conducted according to the following procedure.

Test Description: Test oils were "aged" by accumulating
10 approximately 400 over- the- road test miles on the vehicle. The test vehicle was operated on a chassis dynamometer at several conditions including the EPA-505 test cycle, steady state operation at 30 & 55 mph@ level road load and 55 mph@ increased load (2.5% road grade). NOx emissions were measured
15 using a portable Horiba NOx meter and data were downloaded into a data logger. Three test runs were conducted at each condition on each oil. The results of the steady state operations are provided in Figure 3. The increased load is designated as Hi-load. The result of the EPA-505 test cycle
20 is provided in Figure 4.

5

C L A I M S

1. Lubricating oil composition useful for a diesel engine comprising:

a base oil; and,

one or more compounds represented by the formula:

10

$R - (N = C = O)_x$

wherein R is a hydrocarbyl group having 4 to 30 carbon atoms, and x is an integer of 1 to 4, present in an amount of at least 0.1% by weight up to 5% by weight based on the weight of the lubricating oil composition.

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2. Lubricating oil composition according to claim 1 wherein x is 1 or 2.

3. Lubricating oil composition according to claims 1 or 2, wherein the compound is methylene diphenyl diisocyanate.

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4. Lubricating oil composition according to any one of claims 1 to 3, wherein the compound is present in an amount of at least 0.5% by weight based on the weight of the lubricating oil composition.

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5. A method of operating a diesel engine comprising: introducing into the diesel engine a lubricating oil composition according to any one of claims 1 to 4; and operating the engine.

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6. A method of operating a diesel engine comprising: an engine body; a combustion chamber formed in the engine body for containing a mixture of fuel and air; a plurality of cylinders formed in the engine body; and a respective piston mounted in each of said plurality of cylinders for reciprocal movement through successive exhaust and intake strokes, each

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5 respective piston defining a combustion chamber for
containing a mixture of fuel and air comprising:

introducing, into the combustion chamber, diesel fuel
and air;

delivering a lubricating oil composition according to
10 any one of claims 1 to 4 to the cylinders; and

compressing the diesel fuel in the combustion chamber to
ignition with the piston thereby producing an exhaust gas.

7. Use of one or more isocyanates as a NO_x reducing agent in
15 a diesel lubricating oil composition comprising a base oil.