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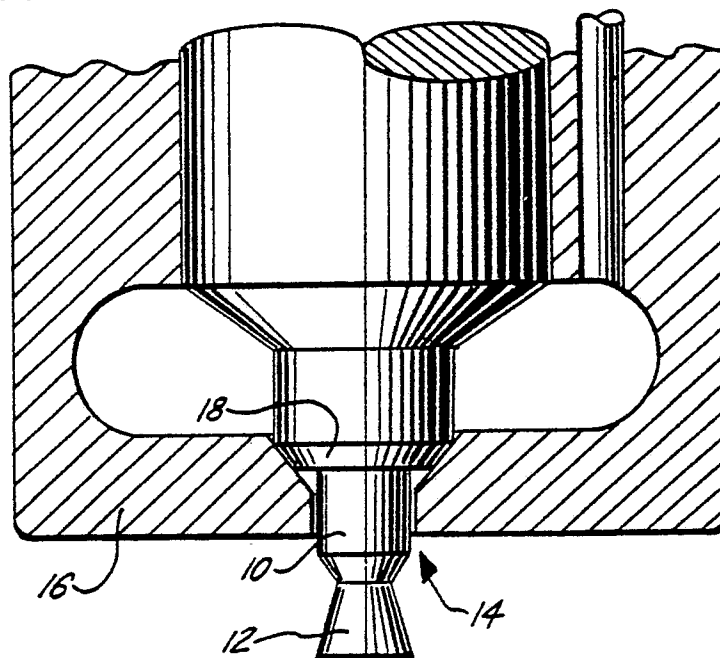
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(54) **Fuel composition and additive concentrates, and their use in inhibiting engine coking.**

(57) Coking in and around the injector nozzles of indirect injection compression ignition engines is reduced by means of distillate fuel into which has been blended suitable concentrations of:

- (a) organic nitrate ignition accelerator,
- (b) hydrocarbonyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, and
- (c) N,N'-disalicylidene-1,2-diaminopropane. Additive concentrates can be formulated using such additive combinations.



FUEL COMPOSITION AND ADDITIVE CONCENTRATES, AND THEIR USE IN INHIBITING ENGINE COKING

The invention relates to compression ignition fuel compositions and additive mixtures of organic nitrate ignition accelerator, hydrocarbyl amine and N,N'-disalicylidene-1,2-diaminopropane, in amounts sufficient to resist the coking tendencies of compression ignition fuel compositions when used in the operation of indirect injection diesel engines.

5 Throttling diesel nozzles have recently come into widespread use in indirect injection automotive and light-duty diesel truck engines, i.e., compression ignition engines in which the fuel is injected into and ignited in a prechamber or swirl chamber. In this way, the flame front proceeds from the prechamber into the larger compression chamber where the combustion is completed. Engines designed in this manner allow for quieter and smoother operation. The Figure of the Drawing illustrates the geometry of the typical
10 throttling diesel nozzle (often referred to as the "pintle nozzle").

Unfortunately, the advent of such engines has given rise to a new problem, that of excessive coking on the critical surfaces of the injectors that inject fuel into the prechamber or swirl chamber of the engine. In particular, and with reference to the accompanying Figure, the carbon tends to fill in all of the available corners and surfaces of the obturator 10 and the form 12 until a smooth profile is achieved. The carbon also
15 tends to block the drilled orifice 14 in the injector body 16 and fill up to the seat 18. In severe cases, carbon builds up on the form 12 and the obturator 10 to such an extent that it interferes with the spray pattern of the fuel issuing from around the perimeter of orifice 14. Such carbon build up or coking often results in such undesirable consequences as delayed fuel injection, increased rate of fuel injection, increased rate of combustion chamber pressure rise, and increased engine noise, and can also result in an excessive
20 increase in emission from the engine of unburned hydrocarbons.

While low fuel cetane number is believed to be a major contributing factor to the coking problem, it is not the only relevant factor. Thermal and oxidative stability (lacquering tendencies), fuel aromaticity, and such fuel characteristics as viscosity, surface tension and relative density have also been indicated to play a role in the coking problem.

25 An important contribution to the art would be a fuel composition which has enhanced resistance to coking tendencies when employed in the operation of indirect injection diesel engines.

This invention provides distillate fuel for indirect injection compression ignition engines containing a combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (c) N,N'-disalicylidene-1,2-diaminopropane, the combination being present in
30 an amount sufficient to suppress and preferably to minimize coking, especially throttling nozzle coking, in the prechambers or swirl chambers of indirect injection compression ignition engines operated on such fuel.

Included in the invention is additive fluid concentrate for use in distillate fuels and which contains a combination as defined above.

Since the invention also embodies the operation of an indirect injection compression ignition engine in a
35 manner which results in reduced coking, a still further embodiment of the present invention is a method of inhibiting coking, especially throttling nozzle coking, in the prechambers or swirl chambers of an indirect injection compression ignition engine, which comprises supplying said engine with a distillate fuel containing a combination as defined above, said combination being present in an amount sufficient to suppress and preferably to minimize such coking in an engine operated on such fuel.

40 A feature of this invention is that the combination of additives utilized in its practice is capable of suppressing coking tendencies of fuels used to operate indirect injection compression ignition engines. Such behavior was exhibited in a series of standard engine dynamometer tests conducted as described in the Example hereinafter.

A wide variety of organic nitrate ignition accelerators, component (a), may be employed in the fuels of
45 this invention. Preferred nitrate esters are the aliphatic or cycloaliphatic nitrates in which the aliphatic or cycloaliphatic group is saturated, contains up to about 12 carbons and, optionally, may be substituted with one or more oxygen atoms.

Typical organic nitrates that may be used are methyl nitrate, ethyl nitrate, propyl nitrate, isopropyl nitrate, allyl nitrate, butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, amyl nitrate, isoamyl
50 nitrate, 2-amyl nitrate, 3-amyl nitrate, hexyl nitrate, heptyl nitrate, 2-heptyl nitrate, octyl nitrate, iso-octyl nitrate, 2-ethylhexyl nitrate, nonyl nitrate, decyl nitrate, undecyl nitrate, dodecyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, cyclododecyl nitrate, 2-ethoxyethyl nitrate, 2-(2-ethoxy-ethoxy)ethyl nitrate, tetra-hydrofuranyl nitrate, and the like. Mixtures of such materials may also be used. The preferred ignition accelerator for use in the fuels of this invention is a mixture of octyl nitrates available as an article of commerce from Ethyl Corporation under the designation DII-3 ignition improver.

The nitrate ignition accelerator--component (a)--should be present in an amount of at least 100 to 1000 PTB (pounds per thousand barrels) - 0.2859 to 2.859 grams per liter - of the base fuel. Preferably, the concentration of the ignition accelerator is 400 to 600 PTB (1.1436 to 1.7154 grams per liter).

It is not believed that there is anything critical as regards the maximum amount of component (a) used in the fuel. Thus, the maximum amount of this component will probably be governed in any given situation by matters of choice and economics.

While a variety of hydrocarbyl amines (b) may be used in the fuel compositions of this invention, a primary aliphatic amine, the aliphatic group of which is tertiary, e.g., an amine of the formula:



wherein R is one or a mixture of tertiary aliphatic groups containing 8 to 18 or more (preferably 12-16) carbon atoms is preferred. Most preferably, these tertiary aliphatic groups are tertiary alkyl groups. It is also preferred that hydrocarbyl amine component (b) include in addition to the above-depicted amine one or more hydrocarbyl amines differing therefrom.

U.S. Pat. No. 3,909,215 gives a description of the various hydrocarbyl amines having from 3 to 60 carbons and from 1 to 10 nitrogens which may be employed in the fuels of this invention. A few additional examples of desirable amines include 2,6-di-*tert*-butyl- α -dimethylamino-*p*-cresol, N-cyclohexyl-N,N-dimethylamine, and N-alkyl-N,N-dimethylamines in which the alkyl group is one or a combination of alkyl groups preferably having 8 to 18 or more carbon atoms.

A particularly preferred hydrocarbyl amine is available commercially from the Rohm and Haas Company under the designation Primene 81R. The Primene 81R is believed to be a mixture of primary aliphatic amines in which the aliphatic groups are predominantly C₁₂ and C₁₄ tertiary alkyl groups.

The fuels of this invention should contain at least 1.5 to 40 PTB (0.00429 to 0.1143 grams/liter) of component (b), the hydrocarbyl amine.

The metal deactivator N,N'-disalicylidene-1,2-diaminopropane (d) is also included in the combination. This compound (80 weight percent active compound in 20 weight percent toluene solvent) is available as an article of commerce from Ethyl Corporation under the designation "Ethyl" MDA.

The fuels of this invention should contain at least 0.2 to 5 PTB (0.00572 to 0.012 grams per liter) of component (c), the metal deactivator, preferably N,N'-disalicylidene-1,2-diaminopropane.

In these fluid compositions, the amount of components (a), (b) and (c) can vary widely. In general, the fluid compositions contain 10 to 97.9% by weight of the organic nitrate ignition accelerator component, 2.0 to 75% by weight of the hydrocarbyl amine and 0.1 to 15% by weight metal deactivator. Typically, from 0.01% by weight up to 1.0% by weight of the combination of the components (a), (b) and (c) will be sufficient to provide good coking-inhibiting properties to the distillate fuel. A preferred distillate fuel composition contains from 0.1 to 0.5% by weight of the combination containing from 50 to 97.9% by weight of the organic nitrate ignition accelerator, from 2.0 to 45% by weight of the hydrocarbyl amine and from 0.1 to 5.0% by weight of the metal deactivator component.

Such fluids in addition to resulting in great convenience in storage, handling, transportation, blending with fuels, and so forth, also are potent concentrates which serve the function of inhibiting or minimizing the coking characteristics of compression ignition distillate fuels used to operate indirect compression ignition engines.

The additive fluids, as well as the distillate fuel compositions of the present invention may also contain other additives such as corrosion inhibitors, antioxidants, metal deactivators, detergents, cold flow improvers, inert solvents or diluents, and the like.

The practice and advantages of this invention will become still further apparent from the following illustrative Example.

EXAMPLE

In order to determine the effect of the fuel compositions of the present invention on the coking tendency of diesel injectors in indirect injection compression ignition engines, use was made of a commercial diesel engine operated on a coking test cycle developed by Institute Francais Petrole and as practiced by Peugeot S. A. The amount of coking together with a quantitative indication of the adverse consequences of such coking was determined by means of (i) injector air flow performance, (ii) emission of unburned hydrocarbons, (iii) engine noise, and (iv) injector deposit ratings. The engine employed in the

tests was a 1982 Peugeot 2.3 liter, 4-cylinder, turbo-charged XD2S diesel engine connected to a Midwest dynamometer through an engine clutch. This engine is equipped with Bosch injectors positioned within prechambers, and is deemed representative of the indirect injection compression ignition engines widely used in automobiles and light-duty trucks.

- 5 The base fuel employed in these engine tests was a commercially-available diesel fuel having a nominal cetane rating of 42. FIA analysis indicated the fuel was composed by volume of 31.5% aromatics, 3.0% olefins and 65.5% saturates. Its distillation range (ASTM D-158) was as follows:

10	Barometer	29.46 inches of Hg	(0.9987 Bars)
	Initial	406°F	207.78°C
	% Evaporated	at °F	at °C
	5	439	226.11
15	10	450	232.22
	15	456	235.56
20	20	463	239.44
	30	480	248.89
	40	499	259.44
25	50	521	271.67
	60	545	285.0
30	70	572	300.0
	80	603	317.22
	85	621	327.22
35	90	643	339.44
	95	678	358.89
40			
	Final	678°F	358.89
45	Recovery	97.5%	
	Residue	2.5%	
	Loss	None	

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Other inspection data on the base fuel were as follows:

Kinematic Viscosity, (ASTM D-445) . . . 3.50 Centistokes, 40°C

Pour Point (ASTM D-97) -26°C

Cloud Point (ASTM D-97) 33°C

55 Flash Point (ASTM D-93) 91°C

Steam Jet Gum 2.4 mg/100 ml

Aniline Point (ASTM D-611) 143.4°F (61.89°C)

Total Sulfur. 0.41 wt. %

Ramsbottom Carbon, % (ASTM D-524) . . . 0.1460 on 10%

Residuum

Gravity (ASTM D-287) 31.8 °API

Specific Gravity @ 25°C 0.86

5 Cetane rating 41

A test blend was prepared from this base fuel. The test fuel contained a combination of

(i) 506 PTB (1.447 grams per liter) of mixed octyl nitrates (a commercial product available from Ethyl Corporation under the designation DII-3 Ignition Improver), (ii) 13.2 PTB (0.0377 grams per liter) of a hydrocarbyl amine available commercially from Rohm and Haas Company under the designation Primene 81R and (iii) 1.7 PTB (0.00486 grams per liter) of "Ethyl" Metal Deactivator, a product of Ethyl Corporation,

10 the active ingredient of which is N,N'-disalicylidene-1,2-diaminopropane.

The Primene 81R is believed to be a mixture of primary aliphatic amines in which the aliphatic groups are predominantly C₁₂ and C₁₄ tertiary alkyl groups.

The manufacturer gives the following typical properties for its "Ethyl" metal Deactivator:

15 Form Liquid

Color Amber

Density, at 68°F

g/ml 1.0672

lb/gal 8.91

20 Active ingredient, wt % 80

Solvent vehicle (toluene), wt % 20

Flash point, open cup, °F 84 (28.89°C)

Fire point, °F 100 (37.78°C)

Solubility

25 In gasoline (Typical) Saturate solution contains 94% MDA

In water, wt. % 0.04

Shell Rotella T, an SAE 30, SF/CD oil was used as the crankcase lubricant.

Before starting each test, new Bosch DNOSD -1510 nozzles were installed using new copper gaskets and flame rings. The fuel line was flushed with the new test fuel composition to be tested and the fuel filter

30 bowl and fuel return reservoir were emptied to avoid additive carry-over from test-to-test.

At the start of each test, the engine was operated at 1000 rpm, light load for 15 minutes. After this warm-up, the engine was subjected to the following automatic cycle:

	<u>Event</u>	<u>RPM</u>	<u>Beam Load</u>	<u>Minutes</u>	<u>EGR</u>
35	1	750	0	4	off
	2	2750	12.0	6	on
40	3	1500	6.2	6	on
	4	4000	16.2	4	off

45 The above 20-minute cycle was repeated 60 times and the test was completed by running the engine at idle for another 30 minutes. The total elapsed time was thus 20.5 hours per test.

When passing from one event to the next event in the above cycle, some time, of course, was required to enable the engine to accelerate or decelerate from one speed to the next. Thus, more specifically, the above cycle was programmed as follows:

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	<u>Segment</u>	<u>Seconds</u>	<u>rpm</u>	<u>Beam Load</u>
	1	2	750	0
5	2	200	750	0
	3	3*	2500	12
10	4	7*	2750	12
	5	350	2750	12
	6	3*	2275	6.2
15	7	7*	1500	6.2
	8	330	1500	6.2
20	9	3*	3500	16.2
	10	7*	4000	16.2
25	11	230	4000	16.2
	12	3*	2000	0
	13	7*	750	0
30	14	30	750	0

* Represents two mode periods for acceleration or deceleration to the next condition.

Hydrocarbon exhaust emissions were measured at the start of each test (after the first 20-minute cycle), at the 6-hour test interval and at the end of the test. These measurements were made at 750, 1000, and 1400 rpm idle. Noise level readings were made at a location three feet from the engine exhaust side. The measurements were made at the start and at the end of the test while operating at three idle speeds, viz., 750, 1000 and 1400 rpm.

After the test operation, the injectors were carefully removed from the engine so as not to disturb the deposits formed thereon. Measurements were made of air flow through each nozzle at different pintle lifts, and pintle deposits were rated using the CRC deposit rating system.

The most significant test results are given in the Table, in which air flow is expressed as cc/min and hydrocarbon emissions as ppm.

TABLE

5	Fuel	Air Flow @ 0.1 mm Lift	Pintle Obturator Deposits (10 = clean)	Noise, DB		Hydrocarbon Emissions	
				EOT*	INCR.	EOT*	Incr.
	Base	36	8.0	83.8	3.0	577	406
10	Test	49	8.4	81.3	2.2	282	51

* Value at end of test; the increase (Incr.) shown is in comparison to the value at start of test.

15 The results presented in the Table show that there were less coking deposits (higher air flow rate and fewer deposits), less engine noise and less hydrocarbon emissions with the fuel of the invention, as compared to the Base Fuel.

20 Claims

1. A distillate fuel composition for indirect injection compression ignition engines containing in an amount sufficient to suppress and preferably to minimize coking in nozzles of indirect injection compression ignition engines operated on such fuel a combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (c) N,N'-disalicylidene-1,2-diaminopropane.

2. A composition as claimed in claim 1, wherein said ignition accelerator is a mixture of octyl nitrates.

3. A composition as claimed in claim 1 or claim 2 wherein the hydrocarbyl amine is of the formula R-NH₂, wherein R is one or more tertiary aliphatic groups containing from 8 to 18 carbon atoms.

30 4. A composition as claimed in claim 3 wherein R is a C₁₂-C₁₆ tertiary aliphatic group.

5. A composition as claimed in claim 3 or claim 4 wherein the tertiary aliphatic group is a tertiary alkyl group.

6. Any modification of a composition as claimed in any one of claims 3 to 5 wherein the hydrocarbyl amine component (b) includes, in addition to an amine of the formula R-NH₂, one or more other hydrocarbyl amines as defined in claim 1.

7. A composition as claimed in any one of claims 1,2 or 6 wherein the hydrocarbyl amine component (b) comprises 2,6-di-*tert*-butyl- α -dimethylamino-*p*-cresol, N-cyclohexyl-N,N-dimethylamine or an N-alkyl-N,N-dimethylamine wherein the alkyl group is one or more alkyl groups having from 8 to 18 carbon atoms.

8. A composition as claimed in claim 1 or claim 2 wherein the hydrocarbyl amine is a mixture of primary aliphatic amines in which the aliphatic groups are predominantly C₁₂ and C₁₄ tertiary alkyl groups.

9. An additive fluid concentrate for use in distillate fuels which contains a combination defined in any one of claims 1 to 8.

10. A method of inhibiting coking on the injector nozzles of an indirect injection compression ignition engine during operation thereof, which method comprises supplying said engine with a distillate fuel composition containing in an amount sufficient to suppress and preferably to minimize such coking in the engine operated on such fuel a combination defined in any one of claims 1 to 8.

Claims for the following contracting state: Austria

50 1. A process for preparing a distillate fuel composition for indirect injection compression ignition engines, which process comprises incorporating in distillate fuel in an amount sufficient to suppress and preferably to minimize coking in the nozzles of indirect injection compression ignition engines operated on such fuel a combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (c) N,N'-disalicylidene-1,2-diaminopropane.

2. A process as claimed in claim 1, wherein said ignition accelerator is a mixture of octyl nitrates.

3. A process as claimed in claim 1 or claim 2 wherein the hydrocarbyl amine is of the formula R-NH₂, wherein R is one or more tertiary aliphatic groups containing from 8 to 18 carbon atoms.

4. A process as claimed in claim 3 wherein R is a C₁₂ -C₁₆ tertiary alkyl group or another C₁₂ -C₁₆ tertiary aliphatic group.

5. A modification of a process as claimed in claim 3 or claim 4 wherein the hydrocarbyl amine component (b) includes, in addition to an amine of the formula R-NH₂, one or more other hydrocarbyl amines as defined in claim 1.

6. A process as claimed in any one of claims 1, 2 or 5 wherein the hydrocarbyl amine component (b) comprises 2, 6-di-tert-butyl- α -dimethylamino-p-cresol, N-cyclohexyl-N,N-dimethylamine or an N-alkyl-N,N-dimethylamine wherein the alkyl group is one or more alkyl groups having from 8 to 18 carbon atoms.

7. A process as claimed in claim 1 or claim 2 wherein the hydrocarbyl amine is a mixture of primary aliphatic amines in which the aliphatic groups are predominantly C₁₂ and C₁₄ tertiary alkyl groups.

8. A process for preparing an additive fluid concentrate for use in distillate fuels, comprising formulating together the components of a combination as defined in any one of claims 1 to 7.

9. A method of inhibiting coking on the injector nozzles of indirect injection compression ignition engines during operation thereof, which method comprises supplying said engine with a distillate fuel composition containing in an amount sufficient to suppress and preferably to minimize coking in nozzles of indirect injection compression ignition engines operated on such fuel a combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (c) N,N'-disalicylidene-1,2-diaminopropane, said combination optionally being as further defined in any one of claims 2 to 7.

10. The use as a distillate fuel additive to inhibit coking on the injector nozzles of indirect compression ignition engines of a combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (c) N,N'-disalicylidene-1,2-diaminopropane, the combination optionally being as further defined in any one of claims 2 to 7.

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