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(54) Fuel compositions 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, and
(b) hydrocarbyl-substituted succinimide or succinamide,
or
(a) organic nitrate ignition accelerator,
(c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, and
(d) N,N'-disalicylidene-1,2-diaminopropane, or
(b) hydrocarbyl-substituted succinimide or succinamide,
(c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens, and
(d) N,N'-disalicylidene-1,2-diaminopropane.

Additive concetrates can be formulated using such additive combinations.

Croydon Printing Company Ltd

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 and hydrocarbyl-substituted succinimide or succinamide, in amounts sufficient to resist the coking tendencies of compression ignition fuel compositions when used in the operation of indirect injection diesel engines.

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 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 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 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.

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.

In accordance with one of its embodiments, this invention provides distillate fuel for indirect injection compression ignition engines containing at least the combination of (a) organic nitrate ignition accelerator, and (b) hydrocarbyl-substituted succinimide, or the combination of (a) organic nitrate ignition accelerator, (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (d) N,N-disalicylidene-1,2-diaminopropane, or the combination of (b) hydrocarbyl-substituted succinimide, (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (d) N,N'-disalicylidene-1,2-diaminopropane, said combinations being separately present in an amount sufficient to minimize coking, especially throttling nozzle coking, in the prechambers or swirl chambers of indirect injection compression ignition engines operated on such fuel.

Another embodiment of the present invention is a distillate fuel additive fluid composition comprising (a) organic nitrate ignition accelerator, and (b) hydrocarbyl-substituted succinimide, or (a) organic nitrate ignition accelerator, (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (d) N,N'-disalicylidene-1,2-diaminopropane or (b) hydrocarbyl-substituted succinimide, (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (d) N,N'-disalicyclidene-1,2-diaminopropane in an amount sufficient to minimize the coking characteristics of such fuel, especially throttling nozzle coking, in the prechambers or swirl chambers of indirect compression ignition engines operated on such fuel.

Since the invention also embodies the operation of an indirect injection compression ignition engine in a 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 at least the combination of (a) organic nitrate ignition accelerator, and (b) hydrocarbyl-substituted succinimide, or the combination of (a) organic nitrate ignition accelerator, (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (d) N,N'-disalicylidene-1,2-diaminopropane or the combination of (b) hydrocarbyl-substituted succinimide, (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (d)

N,N'-disalicyclidene-1,2-diaminopropane, said combinations being separately present in an amount sufficient to minimize such coking in an engine operated on such fuel.

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 Examples I, II and III hereinafter.

A wide variety of organic nitrate ignition accelerators, component (a), may be employed in the fuels of 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 nitrate, 2-amyl nitrate, 3-amyl nitrate, hexyl nitrate, heptyl nitrate, 2-heptyl nitrate, octyl nitrate, isooctyl 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, tetrahydrofuranyl 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 hydrocarbyl-substituted succinimides, component (b) of the fuels of this invention, are well known. They are readily made by first reacting an olefinically unsaturated hydrocarbon of the desired molecular weight with maleic anhydride to form a hydrocarbyl-substituted succinic anhydride. Reaction temperatures of 100-250°C are used. With higher boiling olefinically-unsaturated hydrocarbons, good results are obtained at 200-250°C. This reaction can be promoted by the addition of chlorine. Typical olefins include cracked wax olefins, linear alpha olefins, branched chain alpha olefins, polymers and copolymers of lower olefins. These include polymers of ethylene, propylene, isobutylene, 1-hexene, 1-decene and the like. Useful copolymers are ethylene-propylene copolymers, ethylene-isobutylene copolymers, propylene-isobutylene copolymers, ethylene-1-decene copolymers and the like.

Hydrocarbyl substituents have also been made from olefin terpolymers. Very useful products have been made from ethylene-C_{3-12} alpha olefin - C_{5-12} non-conjugated diene terpolymers; such as ethylene-propylene-1,4-hexadiene terpolymer; ethylene-propylene-1,5-cyclooctadiene terpolymer; ethylene-propylene-norbornene terpolymers and the like.

Of the foregoing, by far the most useful hydrocarbyl substituents are derived from butene polymers, especially polymers of isobutylene.

The molecular weight of the hydrocarbyl substituent can vary over a wide range. It is desirable that the hydrocarbyl group have a molecular weight of at least 500. Although there is no critical upper limit, a preferred range is 500-500,000 number average molecular weight. The more preferred average molecular weight is 700-5,000 and most preferably 900-3,000.

Hydrocarbyl-substituted succinimides and succinamides are made by reaction of the desired hydrocarbyl-substituted succinic anhydride with an amine having at least one reactive hydrogen atom bonded to an amine nitrogen atom. Examples of these are methyl amine, dimethyl amine, n-butyl amine, di-(n-dodecyl) amine, N-(aminoethyl) piperidine, piperazine, N-(3-aminopropyl) piperazine, and the like.

Preferably, the amine has at least one reactive primary amine group capable of reacting to form the preferred succinimides. Examples of such primary amines are n-octyl amine, N,N-dimethyl-1,3-propane diamine, N-(3-aminopropyl) piperazine, 1,6-hexane diamine, and the like.

Hydroxyalkyl amines can also be used to make the succinimide-succinamide components of the invention which contain some ester groups. These amines include ethanol amine, diethanol amine, 2-hydroxypropyl amine, N-hydroxyethyl ethylenediamine and the like. Such hydroxyalkyl amines can be made by reacting a lower alkylene oxide, such as ethylene oxide, propylene oxide or butylene oxide with ammonia or a primary or secondary amine such as ethylene diamine, dethylene triamine, triethylene tetramine, tetraethylenepentamine and the like.

A more preferred class of primary amines used to make the succinimide, succinamide or mixtures thereof are the polyalkylene amines. These are polyamines and mixtures of polyamines which have the general formula

$$H_2N\left(R - NH\right)_nH$$

wherein R is a divalent aliphatic hydrocarbon group having 2-4 carbon atoms and n is an integer from 1-10 including mixtures of such polyalkylene amines.

In a highly preferred embodiment, the polyalkylene amine is a polyethyleneamine containing 2-6 ethyleneamine units. These are represented by the above formula in which R is the group $-CH_2CH_2-$ and n has a value of 2-6.

The amine used to make the succinimide, succinamide or mixture thereof need not be all amine. A mono or poly-hydroxyalcohol may be included in the reaction. Such alcohols can be reacted concurrently with the amine or the two alcohol and amine may be reacted sequentially. Useful alcohols are methanol, ethanol, n-dodecanol, 2-ethyl hexanol, ethylene glycol, propylene glycol, diethylene glycol, 2-ethoxy ethanol, trimethylol propane, pentaerythritol, dipentaerythritol and the like.

Useful amine-alcohol products are described in U.S. 3,184,474; U.S. 3,576,743; U.S. 3,632,511; U.S. 3,804,763; U.S. 3,836,471; U.S. 3,936,480; U.S. 3,948,800; U.S. 3,950,341; U.S. 3,957,854; U.S. 3,957,855; U.S. 3,991,098; U.S. 4,071,548 and U.S. 4,173,540.

The reaction between the hydrocarbyl-substituted succinic anhydride and the amine can be carried out by mixing the components and heating the mixture to a temperature high enough to cause a reaction to occur but not so high as to cause decomposition of the reactants or products or the anhydride may be heated to reaction temperature and the amine added over an extended period. A useful temperature is 100-250°C. Best results are obtained by conducting the reaction at a temperature high enough to distill out water formed in the reaction.

A preferred succinimide-succinamide component is available as an article of commerce from the Edwin Cooper Company under the designation HITEC® E-644. This product comprises a mixture of active ingredients and solvent. Thus, when HITEC® E-644 is used as component (b) in formulating the fuels of this invention, the product as received should be used at a concentration of at least about 40 PTB (pounds per thousand barrels) - 0.11436 grams per liter - to insure that the finished blend contains an adequate quantity of the foregoing succinimide-succinamide ingredient although smaller amounts may be successfully employed.

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 components (a) and (b) used in the fuel. Thus, the maximum amount of these components will probably be governed in any given situation by matters of choice and economics.

The coking-inhibiting components (a) and (b) of the invention can be added to the fuels by any means known in the art for incorporating small quantities of additives into distillate fuels. Components (a) and (b) can be added separately or they can be combined and added together. It is convenient to utilize additive fluid mixtures which consist of organic nitrate ignition accelerator and hydrocarbyl-substituted succinimide-succinamide agents. These additive fluid mixtures are added to distillate fuels. In other words, part of the present invention are coking inhibiting fluids which comprise organic nitrate ignition accelerator and hydrocarbyl-substituted succinimide-succinamide.

Use of 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.

In these fluid compositions, the amount of components (a) and (b) can vary widely. In general, the fluid compositions contain 5 to 95% by weight of the organic nitrate ignition accelerator component and 5 to 95% by weight of the hydrocarbyl-substituted succinimide-succinamide component. Typically, from .01% by weight up to 1.0% by weight of the combination 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 25% to 95% by weight of the organic nitrate ignition accelerator and from 75% to 5% by weight of the hydrocarbyl-substituted succinimide-succinamide component.

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.

Accordingly, a more preferred distillate fuel composition includes a hydrocarbyl amine in combination with the present additives.

While a variety of hydrocarbyl amines 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:

$$R-NH_2$$

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 (c) 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 C_{12} and C_{14} 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 (c), the hydrocarbyl amine.

Accordingly, another embodiment of the present invention is distillate fuel for indirect injection compression ignition engines containing at least the combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide, and (c) hydrocarbyl amine, said combination being present in an amount sufficient to minimize coking, especially throttling nozzle coking in the prechambers or swirl chambers in indirect injection compression ignition engines operated on such fuel.

Also included as a further embodiment of the invention is a distillate fuel additive composition comprising (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide and (c) hydrocarbyl amine in an amount sufficient to minimize the coking characteristics of such fuel, especially throttling nozzle coking in the prechambers or swirl chambers in indirect injection compression ignition engines operated on such fuel.

In general, these additive fuel compositions will contain as much as 50% by weight of the combination of organic nitrate ignition accelerator and hydrocarbyl-substituted succinimide and up to 50% of the hydrocarbyl amine or other additives when they are present.

In a still further embodiment of the invention there is provided 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 at least the combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide and (c) hydrocarbyl amine, said combination being present in an amount sufficient to minimize such coking in an engine operated on such fuel.

Another additive which can be used to advantage in the present invention is a metal deactivator. Examples of these are salicylidene-o-aminophenol, disalicylidene ethylenediamine and disalicylidene propylenediamine. A particularly preferred metal deactivator is N,N'-disalicylidene-1,2-diaminopropane (80 weight percent active in 20 weight percent toluene solvent) which 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 (d), the metal deactivator, preferably N,N'-disalicylidene-1,2-diaminopropane.

Accordingly, another embodiment of the present invention is distillate fuel for indirect injection compression ignition engines containing at least the combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide, (c) hydrocarbyl amine, and (d) N,N'-disalicylidene-1,2-diaminopropane, said combination being present in an amount sufficient to minimize coking, expecially throttling nozzle coking in the prechambers or swirl chambers in indirect injection compression ignition engines operated on such fuel.

Also included as a further embodiment of the invention is a distillate fuel additive composition comprising (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide, (c) hydrocarbyl amine, and (d) N,N'-disalicylidene-1,2-diaminopropane in an amount sufficient to minimize the coking characteristics of such fuel, especially throttling nozzle coking in the prechambers or swirl chambers of indirect injection compression ignition engines operated on such fuels.

In general, these additive fuel compositions will contain as much as 50% by weight of the combination of organic nitrate ignition accelerator and hydrocarbyl-substituted succinimide-succinamide and up to 50% of the combination of hydrocarbyl amine and N,N'-disalicylidene-1,2-diaminopropane or other additives when they are present.

In a still further embodiment of the invention there is provided a method of inhibiting coking, especially throttling nozzle coking in the prechambers or swirl chambers in an indirect injection compression ignition engine which comprises supplying said engine with a distillate fuel containing at least the combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide, (c) hydrocarbyl amine and (d) N,N'-disalicylidene-1,2-diaminopropane, said combination being present in an amount to minimize such coking in an engine operated on such fuel.

In another embodiment of this invention, the coking-inhibiting components (a), (c) and (d) of the invention can be added to the fuels by any means known in the art for incorporating small quantities of additives into distillate fuels. Components (a), (c) and (d) can be added separately or they can be combined and added together. It is convenient to utilize additive fluid mixtures which consist of organic nitrate ignition accelerator, hydrocarbyl amine and metal deactivator agents. These additive fluid mixtures are added to distillate fuels. In other words, part of the present invention are coking inhibiting fluids which comprise organic nitrate ignition accelerator, hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and metal deactivator, preferably N,N'-disalicylidene-1,2-diaminopropane.

In these fluid compositions, the amount of components (a), (c) and (d) 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), (c) and a(d) 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.

In another embodiment of this invention, the coking-inhibiting components (b), (c) and (d) of the invention can be added to the fuels by any means known in the art for incorporating small quantities of additives into distillate fuels. Components (b), (c) and (d) can be added separately or they can be combined and added together. It is convenient to utilize additive fluid mixtures which consist of hydrocarbyl-substituted succinimide-succinamide agents, hydrocarbyl amine and N,N'-disalicylidene-1,2-diaminopropane. These additive fluid mixtures are added to distillate fuels. In other words, part of the present invention are coking inhibiting fluids which comprise hydrocarbyl-substituted succinimide-succinamide, hydrocarbyl amine having from 3 to 60 carbons and 1 to 10 nitrogens, and metal deactivator, preferably N,N'-disalicylidene-1,2-diaminopropane.

In these fluid compositions, the amount of components (b), (c) and (d) can vary widely. In general, the fluid compositions contain 10 to 97.9% by weight of the hydrocarbyl-substituted succinimide-succinamide component, 20 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 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 hydrocarbyl succinimide-succinamide component and from 2.0% to 45% by weight of the hydrocarbyl amine and from 0.1 to 5.0% by weight of the metal deactivator, preferably N,N'-disalicylidene-1,2-diaminopropane.

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

EXAMPLE 1

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.

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:

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

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
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
Cetane rating	41

A test blend was prepared from this base fuel (Fuel A). Fuel A contained a combination of (i) 506 PTB (1.447 grams/liter) of mixed octyl nitrates (a commercial product available from Ethyl Corporation under the designation DII-3 Ignition Improver), (ii) 41 PTB (0.117 gram/liter) of HITEC® E-644, a product of Edwin Cooper, Inc., believed to be a hydrocarbyl succinimide-succinamide made by reacting two moles of a polyisobutenyl succinic anhydride (PIBSA) with one mole of a polyethylene amine mixture having an average composition corresponding to tetraethylene pentamine,

(iii) 14 PTB (0.04 grams/liter) of a hydrocarbyl amine available commercially from Rohm and Haas Company under the designation Primene 81R and (iv) 1.7 PTB (0.00486 grams/liter) of "Ethyl" Metal Deactivator, a product of Ethyl Corporation, the active ingredient of which is N,N'-disalicylidene-1,2-diaminopropane. The manufacturer gives the following typical properties for its HITEC® E-644 product:

Appearance	Dark brown viscous liquid
Nitrogen, wt. %	2.0
Specific Gravity at 60/60°F	0.928
Viscosity at 210°F, cs (98.89°C)	340

The Primene 81R is believed to be a mixture of primary aliphatic amines in which the aliphatic groups are predominantly C_{12} and C_{14} tertiary alkyl groups.

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

Form		Liquid
Color		Amber
Density, at 68°F		
g/ml		1.0672
lb/gal		8.91
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	
In gasoline (Typical)	Saturated 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 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:

Event	RPM	Beam Load	Minutes	EGR
1	750	0	4	off
2	2750	12.0	6	on
3	1500	6.2	6	on
4	4000	16.2	4	off

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:

Segment	Seconds	rpm	Beam Load
1	2	750	0
2	200	750	0
3	3*	2500	12
4	7*	2750	12
5	350	2750	12
6	3*	2275	6.2
7	7*	1500	6.2
8	330	1500	6.2
9	3*	3500	16.2
10	7*	4000	16.2
11	230	4000	16.2
12	3*	2000	0
13	7*	750	0
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 Table I, in which air flow is expressed as cc/min and hydrocarbon emissions as ppm.

TABLE I

Fuel	Air Flow @ 0.1 mm Lift	Pintle Obturator Deposits (10 = clean)	Noise, DB EOT*	Noise, DB INCR.	Hydrocarbon Emissions EOT*	Hydrocarbon Emissions Incr.
Base	36	8.0	83.8	3.0	577	406
A	38	8.6	81.4	1.9	275	143

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

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

EXAMPLE II

A test blend was prepared from the base fuel of Example I (Fuel B). Fuel B 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, the active ingredient of which is N,N'-disalicylidene-1,2-diaminopropane.

The test engine was operated under the same conditions as those of Example I.

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

TABLE II

Fuel	Air Flow @ 0.1 mm Lift	Pintle Obturator Deposits (10 = clean)	Noise, DB EOT*	Noise, DB INCR.	Hydrocarbon Emissions EOT*	Hydrocarbon Emissions Incr.
Base	36	8.0	83.8	3.0	577	406
B	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.

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

EXAMPLE III

A test blend was prepared from the base fuel of Example I (Fuel C). Fuel C contained a combination of (i) 41 PTB (0.117 grams per liter) of HITEC® E-644, a product of Edwin Cooper, Inc., believed to be a hydrocarbyl succinimide-succinamide made by reacting two moles of a polyisobutenyl succinic anhydride (PIBSA) with one mole of a polyethylene amine mixture having an average composition corresponding to tetraethylene pentamine, (ii) 14 PTB (0.04 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, the active ingredient of which is N,N'-disalicylidene-1,2-diaminopropane.

The test engine was operated unde the same conditions as those of Example I. The most significant test results are given in Table III, in which air flow is expressed as cc/min and hydrocarbon emissions as ppm.

TABLE III

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
C	40	8.5	83.2	3.0	513	278

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

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

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 and (b) hydrocarbyl-substituted succinimide or succinamide, and/or the combination of (a) organic nitrate ignition accelerator, (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (d) N,N'-disalicylidene-1,2-diaminopropane, and/or the combination of (b) hydrocarbyl-substituted succinimide or succinamide, (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (d) 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 said hydrocarbyl-substituted succinimide is an olefin polymer substituted succinimide wherein said olefin polymer substituent has an average molecular weight of 500-500,000.

4. A composition as claimed in claim 3, wherein olefin polymer substituent is a polyisobutene substituent having an average molecular weight of 700-5,000.

5. A composition as claimed in claim 3 or claim 4, wherein the succinimide portion is derived from a polyalkyleneamine having the formula

$$H_2N \leftarrow R - NH \rightarrow_n H$$

wherein R is a divalent aliphatic hydrocarbon group having 2-4 carbon atoms and n is an integer from 1-10 including mixtures of said polyaklyene amines.

6. A composition as claimed in claim 5, wherein said polyalkyleneamine is a polyethyleneamine having 2-6 ethylene amine units.

7. A composition as claimed in any one of claims 1 to 6 containing in an amount sufficient to suppress and preferably to minimize coking on the nozzles of indirect injection compression ignition engines operated on such fuel at least the combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide or succinamide, and (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens.

8. A composition as claimed in claim 7 also containing (d) N,N'-disalicylidene-1,2-diaminopropane.

9. An additive fluid concentrate for use in distillate fuels containing at least one of the combinations 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 at least one of the combinations defined in any one of claims 1 to 8.

CLAIMS FOR AUSTRIA:

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 the combination of (a) organic nitrate ignition accelerator and (b) hydrocarbyl-substituted succinimide or succinamide, and/or the combination of (a) organic nitrate ignition accelerator, (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (d) N,N'-disalicylidene-1,2-diaminopropane, and/or the combination of (b) hydrocarbyl-substituted succinimide or succinamide, (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens and (d) 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 said hydrocaryl-substituted succinimide is an olefin polymer substituted succinimide wherein said olefin polymer substituent has an average molecular weight of 500-500,000.

4. A process as claimed in claim 3, wherein said olefin polymer substituent is a polyisobutene substituent

having an average molecular weight of 700-5,000.

5. A process as claimed in claim 3 or claim 4, wherein the succinimide portion is derived from a polyalkyleneamine having the formula

$$H_2N \leftarrow R - NH \rightarrow_n H$$

wherein R is a divalent aliphatic hydrocarbon group having 2-4 carbon atoms and n is an integer from 1-10 including mixtures of said polyalkylene amines.

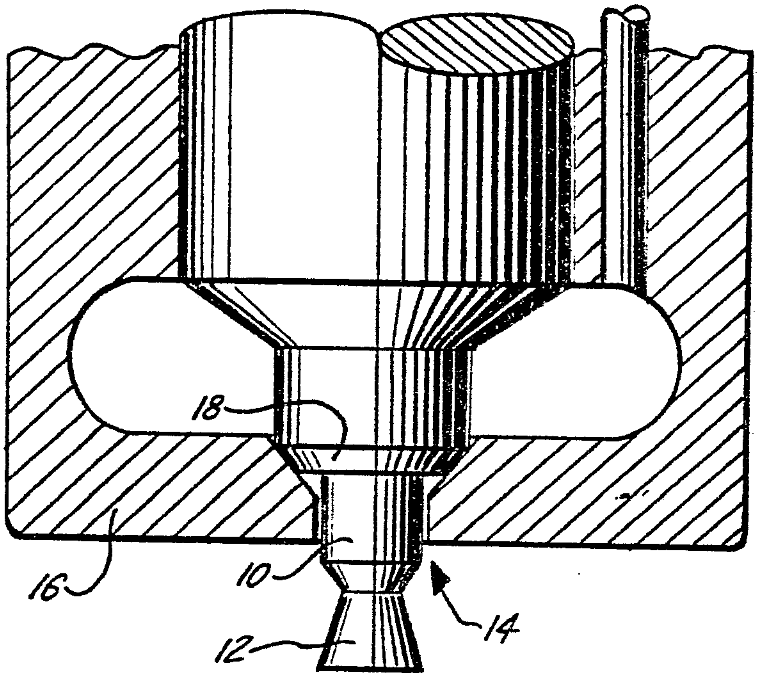
6. A process as claimed in claim 5, wherein said polyalkyeneamine is a polyethyleneamine having 2-6 ethylene amine units.

7. A process as claimed in any one of claims 1 to 6, wherein said fuel has incorporated therein in an amount sufficient to suppress and prerably minimize coking on the nozzles of indirect injection compression ignition engines operated on such fuel at least the combination of (a) organic nitrate ignition accelerator, (b) hydrocarbyl-substituted succinimide or succinamide and (c) hydrocarbyl amine having from 3 to 60 carbons and from 1 to 10 nitrogens.

8. A process as claimed in claim 7, wherein, in addition to components (a), (b) and (c), (d) N,N-disalicylidene-1,2-diaminopropane is incorporated in said fuel.

9. A process for preparing an additive fluid conentrate for use in distillate fuels comprising formulating together the components of at least one of the combinations defined in any one of claims 1 to 8.

10. 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 which has been prepared either by a process as claimed in any one of claims 1 to 8 or by mixing untreated distillate fuel with an additive fluid concentrate which has been prepared by a process as claimed in claim 9.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