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(54) New stabilized fuel composition

(57) This invention is related to a new fuel composition which incorporates a chelating agent capable of stabilizing said fuel against the degradation thereof under working conditions and exposure to contamination by metals observed in the new combustion facilities and engines.

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Description

FIELD OF THE INVENTION

[0001] This invention is related to a new fuel composition which incorporates a chelating agent capable of stabilizing said fuel against the degradation thereof under working conditions and exposure to contamination by metals observed in the new combustion facilities and engines.

PREVIOUS STATE-OF-THE-ART

[0002] Liquid fuels are used widely in industry for transport or furnaces. They are mostly obtained from oil refining, although they may incorporate components from other sources, for example biofuels.

[0003] The stability of the oil fractions and the new fuel components is a property essential to ensuring their appropriate use. And guaranteeing this property is a highly difficult task, especially considering the wide variety of fuel compositions, depending upon their sources and the manner in which they are obtained.

[0004] Numerous additives designed to solve the problems related to hydrocarbon instability currently exist on the market, with different formulations incorporating a complex balance of antioxidants, metal deactivators, neutralizers, detergents and dispersants. Most degradation routes lead to insoluble products, dispersants therefore usually being effective for alleviating this problem. However, there are rubber-forming routes which require an antioxidant to be avoided. In this regard, stabilizing additives exert an influence by neutralizing the acids resulting from oxidation. Other factors causing the speed-up of the oxidation mechanisms are metals (ex. Zn or Cu), such that metal deactivators are also a major factor controlling the degradation mechanisms.

[0005] Metal deactivators are compounds complexing the metals dissolved in the hydrocarbons, preventing the metal ions from initiating or catalyzing the radicalary reactions responsible for said oxidation. The metal passivating compounds which laminate the metal surfaces for prevent their corrosion are also sometimes termed metal deactivators. These compounds, although having a secondary effect on the stability on reducing the solubility of the metals, do not inhibit the catalytic effect thereof for the degradation reactions.

[0006] The use of metal deactivators and antioxidants in gasoline, kerosene and lubricants is mentioned in resources as detailed hereinabove. This is not the case of gas-oils, because the customary consequences of the degradation thereof has been sufficiently remedied to date with the use of dispersants, avoiding the complex use of other products. The use of this type of compounds in gas-oils has always been highly limited, given the complex nature of this fraction.

[0007] The conventional scenario of medium distillates, the stability of which had been reasonably remedied with dispersants, is changing fast. Refineries now need to achieve progressively higher conversion ratios by incorporating currents which have undergone thermal or catalytic stress, their stability differing from the direct distillation currents. The environmental requirements are progressively greater; the permitted maximum sulfur contents are being drastically reduced, increasing the harshness of the hydrotreatment. This process eliminates natural antioxidants in the fuel, where sulphur is also included. Lastly, the modifications in the new combustion facilities and engines favor the presence of metal contaminants, with higher working temperatures and pressures.

[0008] Fuel formulations are progressively more variable as a result of the new oil refining processes. The combined presence of direct distillation and conversion currents at different hydrotreatment levels is progressively more frequent and increases this variability to an even greater degree. The fuel compositions may therefore vary within broad ranges, having highly variable contents in critical compounds such as olefins, diolefins, sulfur and nitrogen heteroatoms, metals, etc. As a result of all of the above, the response of the stabilizers in medium distillates, especially in gas-oils, is highly complex and hardly foreseeable.

[0009] Metals have recently been found to be present in fuels. In a sampling process conducted in 2003 on 78 commercial samples in Spain, the amount of said metals (Cu+Zn) was found to total up to 0.2 mg per kilo of fuel. In addition thereto, the high temperature of the new injection systems has been detected as capable of causing a high solution of Cu up to levels in excess of 1 ppm. These levels of high-temperature metal dissolution have been simulated in high-temperature laboratory tests, the concentrations determined in the field having been found to exist.

[0010] The use of antioxidants and metal deactivators is stated in resources in kerosene-type medium distillates with sulfur contents of over 350 mg/kg (up to 3000 mg/kg). Sulfur being present is essential, given that it is a natural antioxidant. However, the use thereof in diesel fuel is extremely rare, and the effectiveness of these components varies when the sulfur content is less than 350 mg/kg (European legislation since 1999). The response of gas-oil to these additives still differs even more as the sulfur is reduced, being totally different on completely eliminating this element (sulfur content below 10 mg/kg). The EN-590 specification requires content of less than 50 mg/kg in all automotive gas-oils as of 2005 and of less than 10 mg/kg as of 2009.

[0011] The way in which fuels are used is critical, given that the presence of certain factors such as light, dissolved metals, oxygen or the temperature accelerates the destabilizing of the fuel, which entails the forming of insoluble substances which could have a bearing on proper working order (clogging, corrosion, build-up). The evolution of the uses of this fuel requires improving the resistance thereof to the degradation processes.

[0012] In the case of heating fuels, the evolution of their formulations has also been in conjunction with the evolution of the facilities where it is burned. The choice taken was that of a massive incorporation of copper pipes in the facilities, which facilitates the incorporation of copper into the fuel, to which a high recirculation rate to the fuel tank is also added. Additionally, the use of translucent materials for the storage tanks has likewise become widespread, which allows sunlight to act on the fuels. All of the above could help to increase the inestability of the fuels. Lastly, the injection systems have become progressively more complex, thus making fuel stability a critical property for the proper functioning thereof.

[0013] In the case of diesel fuels, another important factor is the evolution of the new engines, with injection systems based on a pump injector and common rail. These systems are highly critical to insolubles and run at high temperatures. The study of the fuels on the market and of the dissolution of metals at high temperatures reveals the presence of metals which catalyze the degradation reactions. The presence of these catalysts and the high working temperatures degrade the fuel and give rise to the formation of insoluble residue which causes the fuel injection to malfunction.

[0014] It is advisable to provide a solution to this type of contaminations and to protect the fuel. To this end, advantage can be taken of the experience acquired in other hydrocarbons and other uses different from combustion.

[0015] Numerous sources make reference to the use of metal deactivators in naphthas. For example, di-(2-hydroxybenzal)-ethylendiamine (US 2284267, US 2181121 and US 2181122) and derivatives of N,N'-di-(3-alkenyl-salicylidene)-diaminoalkane (US 3071451) as a Cu deactivator in gasoline. Products of this type have a marked filming nature, their effectiveness on reducing the catalytic activity of metals is limited.

[0016] The DEF-STAN 91-91 specification indicates that aviation kerosene may incorporate an antioxidant in a concentration within the 17-24 mg/l range and an N,N'-disalicylidene-1,2-propanediamine metal deactivator in a concentration of < 2 mg/l. This is the only metal deactivator permitted in kerosenes and the only one used in other medium distillates. The use of N,N'-disalicylidene-1,2-propanediamine in kerosene is described in several publications (Pande, S.G. et al. in 6th International Conference on Stability and Handling of Liquid Fuel, Canada, 211-230 (1997) and Cyrus, P.H. in 6th International Conference on Stability and Handling of Liquid Fuel, Canada, 51-59 (1997)). In the article published by Chusei, C.C. et al. in Applied Surface Science, USA, 153 23-24 (1999), it is proven how the breakdown thereof may take place at temperatures in excess of 350°C.

[0017] Triazoles and benzotriazoles are used in motor oils for the purpose of prevent corrosion related to the Pb in presence of metals (Cu, brass and bronze) as stated in US patent 0038835 A1. The proportioning used is quite high (2000 ppm). Patent WO 03/004476 A1 also states these products in high proportions (200-1000ppm) as deactivators against Cu and Fe, preferably in lubricant bases for the manufacture of any type of fluid subject to coming into contact with metal surfaces. Other type of deactivators used in lubricants which are described in the Fuels and Lubricants Handbook (Totten, G.E., ASTM International, USA (2003) are lecithin, heterocyclic compound derivatives (thiadiazole, imidazole and pyrazole) and citric and gluconic acid derivatives.

[0018] The use of gluconic acid has been analyzed in depth given the interest in this patent. It is used as a metal and amine captor in refinery processes (WO 2004020553) and as a raw material for lubricants (US 5773391, JP 61031213), for corrosion inhibitors (US 4892671) and for sulfur recovery from natural gas (US 2004192995). In no case has it been used as a metal deactivator for improving the stability of a medium distillate.

[0019] The use of other Cu, Fe, Co and Cr deactivators, such as 1,1,1-tris-(salicylidenaminomethyl)-alkanes, are described in US patent 3843536. The effectiveness of these deactivators is solely demonstrated in gasoline and in lubricant oils in the presence of high concentrations of metals (respectively 8 and 18 ppm) and at high treatment proportioning with deactivator (100-1000 ppm). Nevertheless, these compounds function in a markedly filming manner, as revealed by the high proportions in which they are used.

[0020] N,N'-disalicylidene-1,2-propanediamine is also used in automotive gas-oil, as is stated in patent EP 0476197 A1. This patent is related to a formulation comprised mainly of a deactivator and an agent for improving the low-temperature stability of the additive. The effectiveness of said additive in the presence of Cu has not been demonstrated. In US patent 2813080, a formulation comprised of an N,N'-disalicylidene-1,2-propanediamine deactivator in combination with a dispersant and a combustion enhancer is described. The effectiveness of said formulation in the presence of metals is demonstrated only in the ASTM D-665 test (corrosion related to steel) where the function of the metal deactivator is as a filming agent and not a metal complexing agent.

[0021] It is highly advisable to broaden the application of the metal deactivators to the field of fuels and, more specifically, to the field of gas-oils. It is necessary in low-sulfur automotive gas-oils, which require a greater stability capable of withstanding the high temperatures reached in the new-generation combustion engines and the metal contamination detected in these systems. It is also necessary for the heating gas-oils, due to the progressive incorporation of conversion fractions and the impact which copper and sunlight have on the boiler facilities, the mechanisms (filters and pumps) of which are capable of tolerating a lesser degree of contamination and build-up.

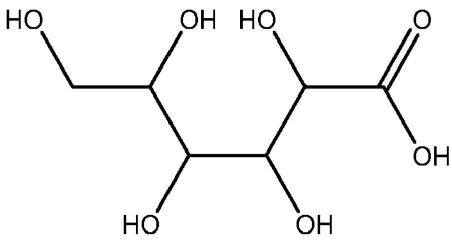
[0022] The limited availability of N,N'-disalicylidene-1,2-propanediamine has given rise to the need of seeking alternative products affording the possibility of diversifying the source of this component. In addition thereto, an opportunity has been found of enhancing the stabilizing effectiveness on certain low-sulfur gas-oil formulations.

[0023] As a result of all of the above, an alternative metal deactivator to N,N'-disalicylidene-1,2-propanediamine has been found for gas-oils and fuels in general which also improves upon some deficiencies thereof.

EXPLANATION OF THE INVENTION

[0024] The inventors of the present invention have developed an alternative composition capable of stabilizing fuels by adding a certain amount of a chelating agent which is capable of forming complexes with the metal ions, inhibiting the catalytic effect thereof and checking the formation of insoluble substances which could have an effect on the proper working order of the engines and boilers (clogging, corrosion, build-up).

[0025] According to one aspect of the present invention, a new fuel composition is provided in which the chelating agent is the compound in Formula I:



I.

or any of the salts thereof. Gluconic acid is included in Formula I.

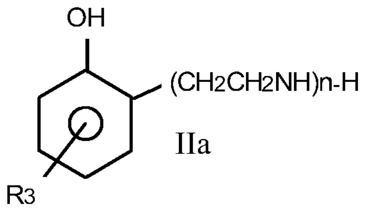
[0026] In this invention, an assessment has been made of the effectiveness of gluconic acid in different proportions, ranging from 1 to 100 mg per kilogram of fuel.

[0027] In one preferred embodiment of the following invention, the fuel is automotive, agricultural or heating gas-oil.

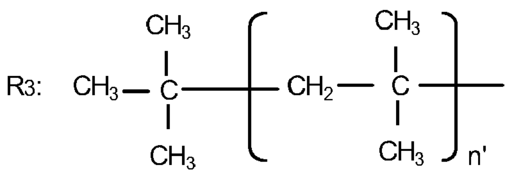
[0028] In another preferred embodiment of the following invention, the composition described comprises 2-50 mg of Formula 1 compound per kilogram of fuel.

[0029] In some cases, a dispersant (DISP) is used for improving the stability of the fuel by preventing the agglomeration of insolubles and the depositing thereof.

[0030] Therefore, the composition described in the following invention may also comprise a dispersant such as, for example but without being limited to, a Mannich base or the derivatives thereof, represented by the following Formula IIa:



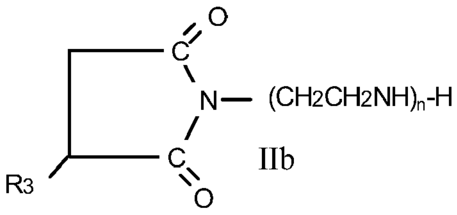
IIa



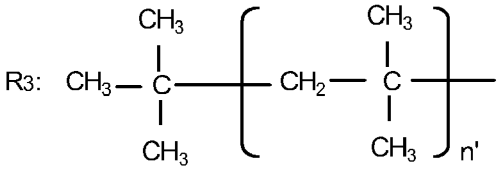
$$R_3:\ CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\left[CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right]_{n'}$$

where n ranges from 1 to 10, both included and n' ranges from 10 to 100, both included.

or a poly-isobutenesuccinimide or the derivatives thereof represented by the following formula IIb:



IIb

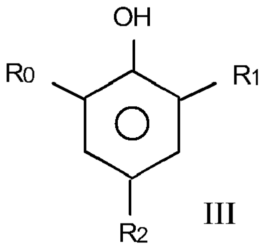


where n ranges from 1 to 10 and n' ranges from 10 to 100, or any mixture of these two dispersants or the derivatives thereof.

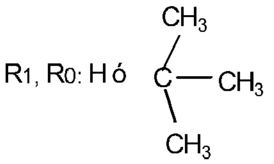
[0031] The dispersant added to the composition described in the present invention is used in a proportion ranging from 10 to 1000 mg per kilogram of fuel, more preferably from 50 to 300 mg per kilogram of fuel.

[0032] An antioxidant may also be added to the composition described in the following invention for the purpose of enhancing the stability of the fuel, particularly of low-sulfur gas-oils or in absence of this natural antioxidant.

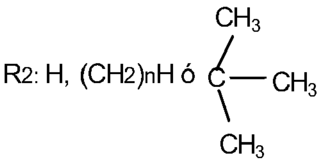
[0033] Thus, the composition described in the following invention may also comprise an antioxidant such as, for example but without being limited to the compounds in formula III:



III



R_1, R_0: H ó $C(CH_3)_3$



R_2: H, $(CH_2)_nH$ ó $C(CH_3)_3$

where n ranges from 1 to 5, all inclusive.

[0034] In a second aspect of the present invention, a method for obtaining the fuel composition described hereinabove is provided, consisting of the following stages:

a) formulating a fuel, preferably an automotive, agricultural or heating gas-oil, and

b) Adding a quantity of the compound of Formula I, previously disclosed, to the fuel prepared in a)

The quantity of the compound of Formula I used is preferably 1 to 100 mg per kilogram of fuel, and more preferably 2 to 50 mg per kilogram of fuel.

[0035] In a preferred embodiment of the method of the present invention, the addition of a polyisobutenesuccinimide type dispersant according to Formula IIb described hereinabove and preferably proportioned at 10 to 1000 mg per kilogram of fuel and more preferably, 50 to 300 mg per kilogram of fuel is included.

[0036] One final aspect of the present invention provides the use of the Formula I compound described hereinabove for the stabilization of a fuel.

[0037] More preferably, the use of the Formula I compound described in the present invention for the stabilization of a fuel, in which said fuel is preferably automotive, agricultural or heating gas-oil.

[0038] In the present invention, the term "fuel" includes the liquid fuels intended for producing heat energy or for being used in internal combustion engines for producing mechanical energy.

[0039] The term "multifunctional package" refers to a composition which comprises but is not limited to one or more dispersing, deemulsifying or antifoaming components. This composition may likewise include other components such as stabilizers, anti-rust additives or cetane improvers.

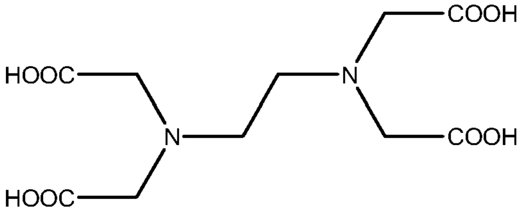
[0040] In the present invention, all of the technical and scientific terms are of the same meaning as that commonly understood by an expert in the field to which the invention pertains. Throughout the description and the claims, the word "comprises" and the variations thereon are not intended to exclude other technical features, components or steps. For the person skilled in the art, other objects, advantages and characteristics of the invention will be implied in part from the description and in part from the practice of the invention. The following examples and drawings are provided for illustrative purposes and are not intended to be limiting of the present invention.

DETAILED EXPLANATION OF EMBODIMENTS

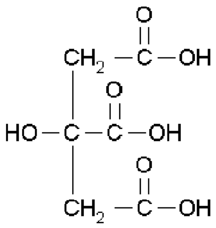
[0041] The invention will be illustrated in following by means of some tests conducted by the inventors revealing the stability of the new composition described as an alternative to other compositions currently existing in the state-of-the-art.

[0042] In example 1, a comparison is drawn between gluconic acid (Formula I) and different products having a chelating capacity, at 5 mg of product per kilogram of gas-oil. The different compounds compared are detailed in following:

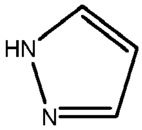
- Ethylendiaminotetracetic acid



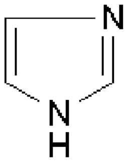
- Citric acid



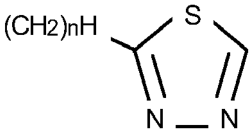
- Pyrazole



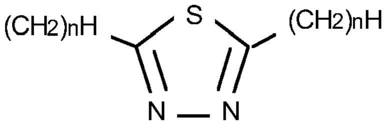
- Imidazole



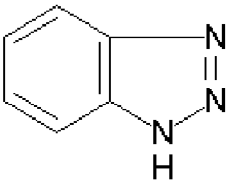
- Monoalkyl thiadazoles



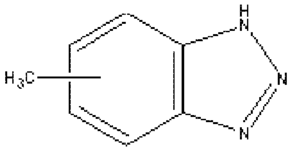
- Dialkyl thiadazoles



- Benzoltriazol



- Tolyltriazol



[0043] The best performance is achieved with gluconic acid. The other chelating agents show a worse performance, even going as far as promoting degradation in some of the gas-oil samples evaluated.

[0044] In the following examples, the effectiveness of gluconic acid has been evaluated by comparing it to the metal deactivator authorized for aviation kerosenes (NNDDP: N,N'-disalicylidene-1,2-propanediamine), at different proportions (2-50 mg/kg), in low-sulfur gas-oils (50 and 10 mg/kg), in presence or absence of metal (Cu^{2+}) and in presence or absence of a dispersant (DISP).

[0045] The possible side-effects of the gluconic acid on different properties, such as filterability (internal method), compatibility with additives (proprietary method), antifoaming capacity (dry and wet manual tests, as well as test tube injection, NF-M-07-075), anti-rust properties (ASTM D-665-B; seawater) and emulsion with water (internal method) were also tested.

EXAMPLE 1

Thermal stability in presence of copper.

[0046] A 50 ml sample of gas-oil doped with 1 ppm Cu^{2+} was aged for 90 minutes at 150°C in absence of light. Afterward, the increase in color in the gas-oil was evaluated as a measurement of the absorbance of the sample diluted in a zero-absorbance solvent. The effectiveness of the metal deactivators on three types of gas-oil of different sulfur contents: automotive gas-oil (GDM1005), agricultural gas-oil (GDM1006) and heating gas-oil (GDM239) were evaluated.

Table 1

Gas-oil	MD used	Increase in absorbance
GDM239	None	0.2068
GDM239	B	0.3076
GDM239	C	0.2426
GDM239	Gluconic acid	0.1368
GDM239	E	0.2136
GDM239	F	0.2142
GDM239	G	0.2649
GDM239	H	0.2704
GDM239	I	0.2789
GDM239	J	0.3286
GDM239	K	0.3700
GDM1006	None	0.0741
GDM1006	B	0.0595
GDM1006	C	0.0386
GDM1006	Gluconic acid	0.0269
GDM1006	E	0.0584
GDM1006	F	0.0485
GDM1006	G	0.0652
GDM1006	H	0.0661
GDM1006	I	0.0512
GDM1006	J	0.0427
GDM1006	K	0.0538
GDM1005	None	0.0699
GDM1005	B	0.0462
GDM1005	C	0.0654
GDM1005	Gluconic acid	0.0445
GDM1005	E	0.0421
GDM1005	F	0.0536
GDM1005	G	0.0534
GDM1005	H	0.0599
GDM1005	I	0.0555
GDM1005	J	0.0805

(continued)

Gas-oil	MD used	Increase in absorbance
GDM1005	K	0.0672
MD. Metal deactivator		

EXAMPLE 2

[0047] HLPS detergency. A 250 ml sample of gas-oil was aged at 280°C, 38 bars, in a system similar to that used for determining the kerosene stability (ASTM-D-3241), recirculating the sample for a maximum of 4 hours. Afterward, the load loss through a filter located downstream from the maximum temperature area was evaluated. The Tendency to Deposits Formation (TDF) was determined in terms of the load loss and the time lapsed up to said loss.

Gas-oil	Sulfur content mg/kg	DISP, ml/m3	MD1, mg/kg	MD2, mg/kg	Cu^{2+} content, mg/kg	TDF
G235	50	0	0	0	0	4.7
G235	50	0	0	0	1	15.0
G235	50	600	0	0	1	2.6
G235	50	600	5	0	1	2.1
G235	50	600	0	10	1	1.8
G235	50	600	0	20	1	3.6
G235	50	0	5	0	1	7.5
G235	50	0	0	10	1	8.6
G235	50	0	0	20	1	7.3
G682	10	0	0	0	0	1.3
G682	10	0	0	0	1	2.2
G682	10	600	0	0	1	2.1
G682	10	600	5	0	1	1.1/2.4
G682	10	600	0	10	1	0.2/1.03
G682	10	600	0	20	1	1.3
G682	10	0	5	0	1	1.8
G682	10	0	0	10	1	2.2
G682	10	0	0	20	1	2.8

Table 2

HLPS. Hot Liquid Process Simulator.

MD. Metal deactivator

MD1 N,N'-disalicylidene-propanediamine (NNDDP).

MD2 gluconic acid (GA)

DISP. Multifunctional package with dispersant (25% polyisobutenesuccinimide).This package includes other components such as an antirust additive, antifoaming agent, demulsifying agent and cetane improver.

TDF. Tendency to Deposits Formation

[0048] Gas-oils with 50 and 10 ppm sulfur were used and the effectiveness of the GA in presence of dispersant at 10 ppm was found to be better than that of the NNDDP at 5 ppm (gluconic TDF: 1.1-0.2; NNDDP TDF: 2.4-1.1), see Table 2.

[0049] However, when the proportion of GA was increased up to 20 ppm, the results were worse (TDF: 1.3-3.6). In this test, it was found, in turn, that neither of the two metal deactivators used are effective on their own, in other words, without a dispersant.

EXAMPLE 3

[0050] UOP-835 thermal stability. A 50 ml sample of gas-oil was aged for 90 minutes at 150°C in absence of light. Afterward, the sample was filtered and the increase in color of the gas-oil evaluated as a measurement of the absorbance of the diluted sample and the filter opacity.

Table 3

Gas-oil	Sulfur content, mg/kg	DISP, ml/m3	MD1, mg/kg	MD2, mg/kg	CU^{2+} content mg/kg	Increase in absorbance	Opacity
G388	10	0	0	0	0	0.035	0.00
G388	10	0	0	0	1	0.059	0.06
G388	10	0	0	2	1	0.052	0.02
G388	10	0	0	5	1	0.050	0.04
G388	10	0	0	10	1	0.044	0.02
G388	10	600	0	2	1	0.048	0.03
G388	10	600	0	5	1	0.062	0.02
G388	10	600	0	10	1	0.048	0.02
G388	10	0	2	0	1	0.051	0.04
G388	10	0	5	0	1	0.039	0.03
G388	10	0	10	0	1	0.032	0.03
G388	10	600	2	0	1	0.060	0.02
G388	10	600	5	0	1	0.058	0.03
G388	10	600	10	0	1	0.044	0.03
G235	50	0	0	0	0	0.031	0.01
G235	50	0	0	0	1	0.072	0.04
G235	50	0	0	2	1	0.087	0.03
G235	50	0	0	5	1	0.084	0.02
G235	50	0	0	10	1	0.087	0.02
G235	50	0	0	20	1	0.096	0.01
G235	50	0	0	50	1	0.064	0.00

(continued)

Gas-oil	Sulfur content, mg/kg	DISP, ml/m3	MD1, mg/kg	MD2, mg/kg	CU^{2+} content mg/kg	Increase in absorbance	Opacity
G235	50	600	0	2	1	0.073	0.01
G235	50	600	0	5	1	0.072	0.02
G235	50	600	0	10	1	0.092	0.01
G235	50	600	0	20	1	0.080	0.01
G235	50	600	0	50	1	0.096	0.01
G235	50	0	2	0	1	0.056	0.01
G235	50	0	5	0	1	0.051	0.01
G235	50	0	10	0	1	0.027	0.02
G235	50	600	2	0	1	0.054	0.02
G235	50	600	5	0	1	0.049	0.01
G235	50	600	10	0	1	0.02	0.01
G682	10	0	0	0	0	0.017	0.01
G682	10	0	0	0	1	0.045	0.01
G682	10	0	0	2	1	0.040	0.02
G682	10	0	0	5	1	0.040	0.01
G682	10	0	0	10	1	0.041	0.03
G682	10	0	0	20	1	0.045	0.01
G682	10	0	0	50	1	0.044	0.00
G682	10	600	0	2	1	0.028	0.01
G682	10	600	0	5	1	0.035	0.02
G682	10	600	0	10	1	0.035	0.02
G682	10	600	0	20	1	0.036	0.01
G682	10	600	0	50	1	0.035	0.03
G682	10	0	2	0	1	0.036	0.01
G682	10	0	5	0	1	0.027	0.00
G682	10	0	10	0	1	0.009	0.02
G682	10	600	2	0	1	0.030	0.01
G682	10	600	5	0	1	0.029	0.01
G682	10	600	10	0	1	0.025	0.01
G306	50	0	0	0	0	0.016	0.04
G306	50	0	0	0	1	0.118	0.07
G306	50	0	0	2	1	0.096	0.04
G306	50	0	0	5	1	0.112	0.03
G306	50	0	0	10	1	0.132	0.04
G306	50	600	0	2	1	0.090	0.03
G306	50	600	0	5	1	0.102	0.04

(continued)

Gas-oil	Sulfur content, mg/kg	DISP, ml/m3	MD1, mg/kg	MD2, mg/kg	CU^{2+} content mg/kg	Increase in absorbance	Opacity
G306	50	600	0	10	1	0.093	0.04
G306	50	0	2	0	1	0.086	0.03
G306	50	0	5	0	1	0.015	0.04
G306	50	0	10	0	1	0.020	0.01
G306	50	600	2	0	1	0.077	0.03
G306	50	600	5	0	1	0.065	0.02
G306	50	600	10	0	1	0.064	0.02

MD. Metal deactivator

MD1	N,N'-disalicylidene-propanediamine (NNDDAP)
MD2	gluconic acid (GA)

DISP. Multifunctional package with dispersant (25% polyisobutenesuccinimide). This package includes other components such as an antirust additive, antifoaming agent, demulsifying agent and a cetane improver.

[0051] Four 50 and 10 ppm gas-oil samples were used, it was found that, in presence of the dispersant (added as multifunctional package) on the gas-oils with 10 ppm sulfur, the GA at 10 ppm showed better results than the NNDDAP at 5 ppm.
The equivalency ratio, with dispersant, between the NNDDAP and GA would be 5:10 ppm, the GA being more effective on the bases of 10 ppm and the NNDDAP on those of 50 ppm.

EXAMPLE 4

[0052] Oxidation stability A 350 ml sample of gas-oil was aged under the conditions stipulated in standard ISO12205 (16 hours, 95°C, with 3L/h oxygen bubbling) in presence of 1 mg/kg Cu^{2+}. Afterward, the insolubles produced were determined as the sum of filterable (0.8 microns) and adherent forms (washed with trisolvent and evaporation at 160°C), measured in g/m3. The Cu^{2+} was added as a reagent in acetate form.

Table 4

Gas-oil	Sulfur content mg/kg	DISP, ml/m3	MD1, mg/kg	MD2, mg/kg	Cu^{2+} content mg/kg	Total insolubles, g/m^3	Increase in absorbance
G235	50	0	0	0	0	1.7	0.020
G235	50	0	0	0	1	Blocks filter	Not measured
G235	50	0	0	2	1	Blocks filter	0.625
G235	50	0	0	5	1	Blocks filter	0.562
G235	50	0	0	10	1	Blocks filter	0.635
G235	50	0	0	20	1	Blocks filter	0.604
G235	50	0	0	50	1	Blocks filter	0.620
G235	50	600	0	2	1	16.3	0.311
G235	50	600	0	5	1	26.0	0.284
G235	50	600	0	10	1	20.0	0.319

(continued)

Gas-oil	Sulfur content mg/kg	DISP, ml/m3	MD1, mg/kg	MD2, mg/kg	Cu^{2+} content mg/kg	Total insolubles, g/m^3	Increase in absorbance
G235	50	600	0	20	1	8.0	0.145
G235	50	600	0	50	1	61.0	0.329
G235	50	0	2	0	1	Blocks filter	0.505
G235	50	0	5	0	1	11.7	0.149
G235	50	0	10	0	1	6.8	0.045
G235	50	600	2	0	1	11.4	0.344
G235	50	600	5	0	1	4.8	0.038
G235	50	600	10	0	1	2.9	0.041
G682	10	0	0	0	0	6.0	0.011
G682	10	0	0	0	1	448.8	0.344
G682	10	0	0	2	1	249.1	0.349
G682	10	0	0	5	1	286.9	0.387
G682	10	0	0	10	1	250.6	0.367
G682	10	0	0	20	1	176.5	0.369
G682	10	0	0	50	1	187.4	0.395
G682	10	600	0	2	1	33.2	0.241
G682	10	600	0	5	1	20.8	0.224
G682	10	600	0	10	1	15.4	0.153
G682	10	600	0	20	1	10.6	0.089
G682	10	600	0	50	1	32.3	0.317
G682	10	0	2	0	1	260.5	0.425
G682	10	0	5	0	1	354.3	0.391
G682	10	0	10	0	1	4.8	0.029
G682	10	0	20	0	1	6.3	0.025
G682	10	0	50	0	1	5.7	0.036
G682	10	600	2	0	1	9.7	0.216
G682	10	600	5	0	1	9.2	0.240
G682	10	600	10	0	1	12.0	0.031
G682	10	600	20	0	1	6.9	0.028
G682	10	600	50	0	1	6.9	0.046

MD Metal deactivator

MD1	N,N'-disalicylidene-propanediamine (NNDDAP)
MD2	gluconic acid (GA)

DISP. Multifunctional package with dispersant (25% polyisobutenesuccinimide) This package includes other components such as an antirust additive, antifoaming agent, deemulsifying agent and a cetane improver.

[0053] It was found that, on adding GA without a dispersant, to a 10 ppm sulphur content base fuel, the insolubles in the base were reduced to the half (from 448.8 to 187-250 g/m^3) at any additioning proportion (2-50 mg/kg).

[0054] In the cases in which dispersant was added, the gluconic acid showed the best results at 20 ppm (8-11 g/m^3), being effective from 2 ppm and achieving less from 21 g/m3 at 10 ppm. In other words, in this case, no benefit was found from increasing the proportion. Tests were conducted up to 50 ppm.

EXAMPLE 5

[0055] Test 5-1. Light stability. A 50 mL sample of gas-oil was aged at 40°C subjected to constant UV radiation for 48 hours, the resulting insolubles having been evaluated in a manner similar to Test 2, adapting the filter, the filtering equipment and the evaporation to the amount of sample employed.

Table 5-1

Gas-oil	Sulfur content mg/kg	DISP, m/m3	MD1, mg/kg	MD2, mg/kg	Cu^{2+} content mg/kg	Total insolubles, g/m3	Increase in absorbance
G235	50	0	0	0	0	27.1	0.031
G235	50	0	0	0	1	32.2	0.065
G235	50	600	0	0	1	38.0	0.051
G235	50	600	5	0	1	13.2	0.033
G235	50	600	0	10	1	23.0	0.022
G235	50	600	0	20	1	29.9	0.043

MD. Metal deactivator

MD1	N,N'-disalicylidene-propanediamine (NNDDAP)
MD2	gluconic acid (GA)

DISP. Multifunctional package with dispersant (25% polyisobutenesuccinimide). This package includes other components, such as an antirust additive, antifoaming agent, demulsifying agent and a cetane improver.

[0056] The GA at 10 ppm was found to reduce the insolubles to 23 g/m3.

[0057] Test 5-2. DUPONT stability (6 weeks, 43°C). A 350 ml volume of sample was stored at 43°C for 42 days, both the insoluble and the adherent forms and the increase in absorbance having then been quantified.

Table 5-2

Gas-oil	Sulfur content mg/kg	DISP, ml/m3	MD1, mg/kg	MD2, mg/kg	Cu^{2+} content mg/kg	Total insolubles g/m3	Increase in absorbance
G235	50	0	0	0	0	1.7	0.031
G235	50	0	0	0	1	6.6	0.182
G235	50	600	0	0	1	19.5	0.214
G235	50	600	5	0	1	7.5	0.373
G235	50	600	0	10	1	5.9	0.277

(continued)

Gas-oil	Sulfur content mg/kg	DISP, ml/m3	MD1, mg/kg	MD2, mg/kg	Cu^{2+} content mg/kg	Total insolubles g/m3	Increase in absorbance
G235	50	600	0	20	1	7.4	0.353

MD. Metal deactivator

MD1 N,N'-disalicylidene-propanediamine (NNDDAP)

MD2 gluconic acid (GA)

DISP. Multifunctional package with dispersant (25% polyisobutenesuccinimide). This package includes other components, such as an antirust additive, antifoaming agent, demulsifying agent and a cetane improver.

[0058] Both metal deactivators were found to be effective at the proportions tested (NNDDP at 5 ppm and GA at 10 and 20 ppm), having managed to reduce the insolubles formed by the base in presence of copper and dispersant to less than half (from 19.5 g/m3 to < 5.9 g/m3). See Table 5-2.

[0059] Test 5-3: Rancimat stability. Air was made to flow through a sample of gas-oil at 110°C. The fumes given off in the oxidation process, along with the air, were routed through a vessel containing distilled water, where the conductivity was measured, which increases by way of the acids formed during the aging process. The end of the induction period was indicated when the conductivity began to rapidly increase. For the purpose of identifying the progressive destabilization (without any abrupt increase in the production of acids), the length of time having lapsed up to a certain conductivity was also recorded.

[0060] The results of the aforementioned test are provided in the second table (Table 5-3).

Table 5-3

Gas-oil	Sulfur content mg/kg	DISP, ml/m3	MD1, mg/kg	MD2; mg/kg	Cu2+ content mg/kg	Induction period, h	Time for delta kappa 40 microsiemens
G235	50	0	0	0	0	20.7//17.1	21.1//20.8
G235	50	0	0	0	1	6//6.5	3.8//0.6
G235	50	600	0	0	1	15//17.3	8.3//8.1
G235	50	600	5	0	1	17.3//19.3//19.5	7.3//7.3//7.1
G235	50	600	0	10	1	14.9//17.5	10.3//9.5
G235	50	600	0	20	1	20//14.9	8.7//8.2

MD. Metal deactivator

MD1 N,N'-disalicylidene-propanediamine (NNDDAP)

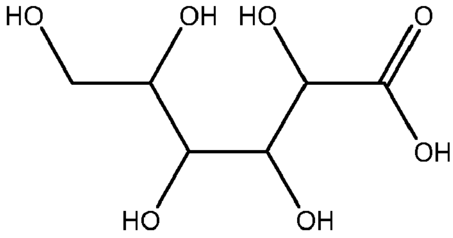
MD2 gluconic acid (GA)

DISP. Multifunctional package with dispersant (25% polyisobutenesuccinimide). This package includes other components, such as an antirust additive, antifoaming agent, demulsifying agent and a cetane improver.

[0061] As shown in the Table, there were no differences in effectiveness between the NNDDP at 5 ppm and the GA at 10 and 20 ppm. The two metal deactivators, in the stated proportions, enhanced the result in presence of copper and dispersant up to values nearing those of the base gas-oil. The gluconic acid shows a better performance than the NNDDP is the progressive destabilization is taken into account.

Claims

1. Fuel composition which comprises a Formula I compound:



I.

or any of the salts thereof.

2. Composition according to Claim 1 hereinabove where the fuel is automotive, agricultural or heating gas-oil.

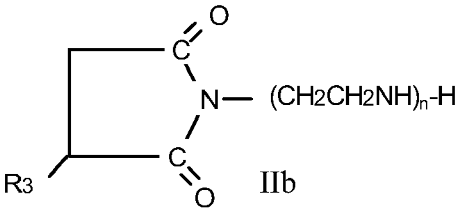
3. Composition according to any of the preceding Claims hereinabove which comprises from 1 to 100 mg of Formula I compound per kilogram of fuel.

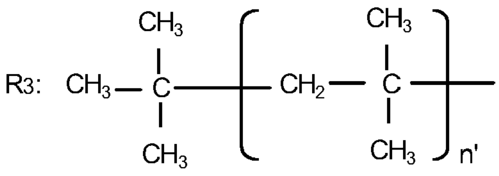
4. Composition according to any of the preceding Claims hereinabove which comprises from 2 to 50 mg of Formula I compound per kilogram of fuel.

5. Composition according to any of the preceding Claims hereinabove which also comprises a dispersant selected from among the following:

   a. a Mannich base or derivatives thereof
   b. a polyisobutenesuccinimide or the derivatives thereof, or
   c. a combination of both.

6. Composition according to Claim 5 hereinabove in which the dispersant is the polyisobutenesuccinimide of Formula IIb:





$$R3:\ CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\left[CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\right]_{n'}$$

where n ranges from 1 to 10 and n' ranges from 10 to 100.

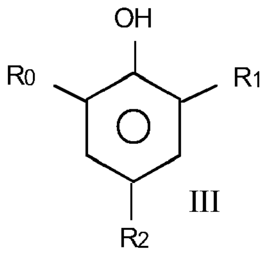
7. Composition according to Claims 5 or 6 hereinabove in which the dispersant is used in a proportion of 10 to 1000 mg per kilogram of fuel.

8. Composition according to Claims 5 or 6 hereinabove in which the dispersant is used in a proportion of 50 to 300

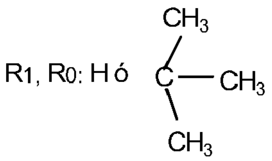
mg per kilogram of fuel.

9. Composition according to any of Claims 5 to 8 hereinabove in which the dispersant is incorporated in conjunction with all of the components of a multifunctional package.

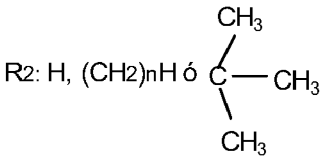
10. Composition according to any of the preceding Claims hereinabove which also comprises a Formula III antioxidant:



III



R_1, R_0: H ó $C(CH_3)_3$



R_2: H, $(CH_2)_n$H ó $C(CH_3)_3$

where n ranges from 1-5.

11. Method for obtaining a fuel composition in accordance with Claim 1 hereinabove which comprises the following stages:

    a. formulating a fuel, and
    b. Adding a Formula I compound to the fuel prepared in a)

12. Method according to Claim 11 hereinabove in which the fuel composition is any of the compositions described in Claims 2 to 10.

13. Use of a Formula I compound for the stabilization of a fuel.

14. Use according to Claim 13 hereinabove in which the fuel is automotive, agricultural or heating gas-oil.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 10 8062

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	28 August 2007	Bertrand, Samuel

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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3

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