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(71) Demandeur/Applicant:  
THE LUBRIZOL CORPORATION, US

(72) Inventeurs/Inventors:  
FORESTER, DAVID R., US;  
ROBERTS, DAVID C., US;  
MANKA, JOHN S., US;  
MALIK, BHARAT B., US

(74) Agent: RIDOUT & MAYBEE LLP

(54) Titre : COMPOSITION DE CONCENTRE D'ADDITIF DE CARBURANT AVIATION, COMPOSITION DE CARBURANT  
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(54) Title: JET FUEL ADDITIVE CONCENTRATE COMPOSITION AND FUEL COMPOSITION AND METHODS  
THEREOF

(57) **Abrégé/Abstract:**

A jet fuel additive concentrate composition comprises a solvent and a combination of components. A fuel composition and methods to improve thermal stability of a jet fuel and to reduce deposits in a jet engine include the jet fuel additive concentrate composition. The improvement in the thermal stability of a jet fuel is synergistic when the combination of components includes a cold-flow improving composition.



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(71) Applicant (*for all designated States except US*): **THE LUBRIZOL CORPORATION** [US/US]; 29400 Lakeland Boulevard, Wickliffe, OH 44092-2298 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **FORESTER, David, R.** [US/US]; 10209 Stonehedge Drive, Concord Township, OH 44077 (US). **ROBERTS, David, C.** [US/US]; 38501 Eagle Nest Lane, Willoughby Hills, OH 44094 (US). **MANKA, John, S.** [US/US]; 10440 Penniman Drive, Chardon, OH 44024 (US). **MALIK, Bharat, B.** [IN/US]; 640 Birch Drive, Euclid, OH 44132-2106 (US).

(74) Agents: **MUNSON, Jeffrey, F.** et al.; The Lubrizol Corporation, 29400 Lakeland Boulevard, Wickliffe, OH 44092-2298 (US).

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(54) Title: JET FUEL ADDITIVE CONCENTRATE COMPOSITION AND FUEL COMPOSITION AND METHODS THEREOF

(57) Abstract: A jet fuel additive concentrate composition comprises a solvent and a combination of components. A fuel composition and methods to improve thermal stability of a jet fuel and to reduce deposits in a jet engine include the jet fuel additive concentrate composition. The improvement in the thermal stability of a jet fuel is synergistic when the combination of components includes a cold-flow improving composition.

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TITLE: JET FUEL ADDITIVE CONCENTRATE COMPOSITION AND  
FUEL COMPOSITION AND METHODS THEREOF

This application claims the benefit of the U. S. Provisional Patent Application No.  
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## BACKGROUND OF THE INVENTION

### FIELD OF THE INVENTION

The present invention relates to a jet fuel additive concentrate composition, a  
fuel composition containing a jet fuel and the jet fuel additive concentrate  
composition, a method that uses the jet fuel additive concentrate composition to  
15 improve the thermal stability of a jet fuel, and a method that uses the fuel composition  
to reduce deposits in a jet engine.

### DESCRIPTION OF THE RELATED ART

Jet fuels experience extremely high temperatures prior to and during  
combustion. Jet fuels are used as a coolant in jet aircraft for various aircraft  
20 subsystems including the engine lubricating oil which can raise the bulk fuel  
temperature to about 220°C. Further, in the combustion system, the fuel can  
experience temperatures up to about 595°C. As a result of these high temperature  
conditions, some fuel degradation can occur leading to deposits in the fuel circulation  
system and combustion system of jet engines. The engine deposits require periodic  
25 maintenance for optimum engine performance. By introducing a thermal stability  
additive composition to a jet fuel, both engine deposits and attendant engine  
maintenance costs can be reduced.

Both U.S. Patent No. 3,652,239 and Japanese Publication No. 2000/080382  
disclose amine derivatives of substituted succinic acylating agents for use in jet fuels.

30 Pentaerythritol esters of polyisobutenylthiophosphonic acids are disclosed in  
U.S. Patent No. 5,725,611 for use in jet fuels for deposit control in jet engine  
components.

Salts of alkylene linked, hydrocarbyl-substituted hydroxyaromatic compounds  
are disclosed in U.S. Patent No. 5,821,202 for use as antifoulants in hydrocarbon  
35 process streams such as jet fuels.



5           Linear oligomers of unsubstituted or substituted phenols and unsubstituted or substituted salicylic acids linked by alkylene groups are disclosed in U.S. Patent Application No. 09/802,500 filed March 9, 2001 for use in jet fuels.

          Cyclic salixarenes are disclosed in U.S. Patent No. 6,270,537 and in International Publication Nos. WO 01/44155 and WO 01/57163 for use in jet fuels for  
10       thermal stability.

          Ethylene vinyl acetate copolymers, reaction products of alkanol amines and hydrocarbyl-substituted acylating agents, and reaction products of hydrocarbyl-substituted phenols and aldehydes are disclosed in International Publication No. WO 01/62874 for use in aviation fuels to lower the freeze point.

15           A combination of an ethylene-vinyl ester copolymer or terpolymer and an alkylphenol-aldehyde resin is disclosed in U.S. Patent No. 5,998,530 for use in jet fuel as a flow improver.

          International Publication No. WO 02/077130 A2 discloses a composition comprising an aviation fuel and a deposit inhibiting compound which does not inhibit  
20       separation of water from the fuel when the fuel is passed through a coalescer.

          It has now been found that certain combinations of additives when added to a jet fuel provide enhanced thermal stability and a reduction in deposit formation and that some of these additive combinations do so synergistically.

#### SUMMARY OF THE INVENTION

25           An object of the present invention is to improve the thermal stability of a jet fuel.

          A further object of the present invention is to reduce deposits in a fuel circulation system and combustion system of a jet engine.

          The objects, advantages and embodiments of the present invention are in part  
30       described in this application and in part are obvious from the application or from the practice of this invention. Therefore, it is understood that the invention is claimed as described or obvious as falls within the scope of the appended claims.

          To achieve the foregoing objects in accordance with the invention as described and claimed herein, a jet fuel additive concentrate composition of the present  
35       invention comprises (A) a solvent suitable for use in a jet fuel; (B) a composition selected from the group consisting of (1) a reaction product of a hydrocarbyl-

5 substituted succinic acylating agent and an amine, an alcohol, or mixtures thereof wherein the hydrocarbyl substituent of (B)(1) has a number average molecular weight of 600 to 3,000; (2) a polyalkenylthiophosphonate ester; (3) a Mannich reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and an amine; and (4) mixtures thereof; and (C) a composition selected from the group consisting of (5) a  
10 metal salt of an oligomeric reaction product of a hydrocarbyl-substituted phenol and an aldehyde; (6) an oligomeric reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and a carboxyl-substituted phenol; and (7) mixtures thereof wherein the solvent is present in the concentrate composition at 20-80 weight %, and each of the compositions for components (B) and (C) is present in the concentrate composition at  
15 1-70 weight %.

In another embodiment of this invention, a fuel composition comprises a jet fuel and the concentrate composition comprising the solvent, the component (B), and the component (C) wherein each of the compositions for components (B) and (C) is present in the fuel composition at 1-1,000 ppm by weight.

20 In a further embodiment of the invention, a method to improve the thermal stability of a jet fuel comprises adding to the jet fuel a thermal-stability improving amount of the concentrate composition comprising the solvent, the component (B), and the component (C).

In yet another embodiment of the present invention, a method to reduce  
25 deposits in a fuel circulation system and combustion system of a jet engine comprises operating the jet engine with the fuel composition comprising jet fuel and the concentrate composition comprising the solvent, the component (B), and the component (C).

Another embodiment of this invention is a jet fuel additive concentrate  
30 composition comprising the solvent, the component (B), the component (C), and (D) a cold-flow improving composition selected from the group consisting of (8) an esterified copolymer of maleic anhydride, styrene, and optionally an alkyl methacrylate; (9) a copolymer of a dialkyl fumarate, a vinyl ester of a carboxylic acid, and optionally a vinyl alkyl ether; (10) a methacrylate polymer prepared from a  
35 mixture of alkyl methacrylate monomers; (11) a copolymer of an olefin selected from the group consisting of olefins having 2 to 12 carbon atoms and mixtures thereof, and



5 a vinyl ester of a carboxylic acid; (12) a polymer prepared from the reaction of an alkylphenol and formaldehyde wherein the alkyl substituent of the alkylphenol has 14 to 60 carbon atoms; (13) a reaction product of a hydrocarbyl substituted acylating agent and an amine selected from the group consisting of an alkanolamine and a polyamine wherein the hydrocarbyl substituent of (D)(13) has 8 to 40 carbon atoms;  
10 and (14) mixtures thereof wherein each of the compositions for component (D) is present in the concentrate composition at 1-70 weight %.

A further embodiment of the present invention is a fuel composition comprising a jet fuel and the concentrate composition comprising the solvent, the component (B), the component (C), and the component (D) wherein each of the  
15 compositions is present in the fuel composition for components (B) and (C) at 1-1,000 ppm by weight and for component (D) at 1-5,000 ppm by weight.

Still another embodiment of this invention is a method to improve the thermal stability of a jet fuel comprising adding to the jet fuel a thermal-stability improving amount of the concentrate composition comprising the solvent, the component (B),  
20 the component (C), and the component (D).

Yet a further embodiment of the present invention is a method to reduce deposits in a fuel circulation system and combustion system of a jet engine comprising operating the jet engine with the fuel composition comprising jet fuel and the concentrate composition comprising the solvent and the components (B), (C) and  
25 (D).

#### DETAILED DESCRIPTION OF THE INVENTION

A jet fuel additive concentrate composition of the present invention comprises (A) a solvent suitable for use in a jet fuel, (B) a composition selected from the group consisting of (1) a reaction product of a hydrocarbyl-substituted succinic acylating agent and an amine, an alcohol, or mixtures thereof wherein the hydrocarbyl  
30 substituent of (B)(1) has a number average molecular weight of 600 to 3,000; (2) a polyalkenylthiophosphonate ester; (3) a Mannich reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and an amine; and (4) mixtures thereof; and (C) a composition selected from the group consisting of (5) a metal salt of an oligomeric reaction product of a hydrocarbyl-substituted phenol and an aldehyde; (6) an  
35 oligomeric reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and a

5 carboxyl-substituted phenol; and (7) mixtures thereof wherein the solvent is present in the concentrate composition at 20-80 weight %, and each of the compositions for components (B) and (C) is present in the concentrate composition at 1-70 weight %.

The solvent of (A) suitable for use in a jet fuel and in the jet fuel additive concentrate compositions and corresponding fuel compositions of the present  
10 invention can be any suitable solvent, typically an organic solvent. Suitable organic solvents include aliphatic and aromatic hydrocarbons comprising xylenes, paraffinic naphtha, aromatic naphtha, or mixtures thereof where the aromatic and paraffinic naphtha typically distills in the range of 130 to 240°C. The solvent generally provides fluidity to the concentrate and homogeneity to the concentrate and fuel compositions.

15 The component (B) can include the reaction product of (B)(1) of a hydrocarbyl-substituted succinic acylating agent and an amine, an alcohol, or mixtures thereof. Throughout this application the term hydrocarbyl represents a univalent group of one or more carbon atoms that is predominately hydrocarbon in nature, but can contain heteroatoms such as oxygen in the carbon chain and can have  
20 nonhydrocarbon and heteroatom-containing groups such as hydroxy, halo, nitro and alkoxy attached to the carbon chain. The hydrocarbyl substituent of the succinic acylating agent can have a number average molecular weight of 600 to 3000, preferably of 650 to 2000, and more preferably of 700 to 1500. The hydrocarbyl substituent can be derived from an olefin. The olefin is typically a polyolefin which  
25 can be a homopolymer derived from a single olefin monomer or a copolymer derived from a mixture of two or more different olefin monomers. The olefin monomer can be an alpha-olefin, an internal olefin or a polyene to include ethylene, propylene, isomers of butene such as isobutylene, isomers of pentene, isomers of decene, and dienes such as isoprene and 1,3-butadiene. A preferred olefin monomer source is a C<sub>4</sub>  
30 refinery stream containing as components butene isomers to include isobutylene. Methods to prepare polyolefins from olefin monomers are well known and include polymerization of the olefin monomers with an acid catalyst such as aluminum trichloride or boron trifluoride. A preferred polyolefin is a highly reactive, high vinylidene content polyisobutylene having at least 70% of its olefinic double bonds as  
35 vinylidene double bonds at a terminal position on the polymer chain. The hydrocarbyl-substituted succinic acylating agent can be prepared by several known



5 methods from an olefin or polyolefin and maleic anhydride or reactive equivalent thereof such as maleic acid and esters of maleic acid. The succinic acylating agent can be prepared by a thermal method that involves temperatures typically ranging from 180 to 250°C and extended reaction hold times. The thermal method is especially useful with a highly reactive, high vinylidene content polyolefin as  
10 described in European Publication No. 355895. Other methods employ various chlorine addition schemes, temperatures normally ranging from 160 to 220°C, and reaction hold times of moderate length as described in U.S. Patent Nos. 4,234,435 and 6,165,235.

The amine of the reaction product of (B)(1) is a composition containing at  
15 least one reactive N-H bond and can include ammonia, monoamines such as butylamine, and polyamines. Polyamines include ethylenediamine, propylenediamine, polyethylenepolyamines such as diethylenetriamine, and polyethylenepolyamine bottoms. Preferred amines include polyethylenepolyamines, polyethylenepolyamine bottoms, and an acid catalyzed condensation product of a  
20 polyamine such as polyethylenepolyamine bottoms and a polyhydroxy-containing compound such as tris(hydroxymethyl)aminomethane as described in U.S. Patent No. 5,569,644.

The alcohol of the reaction product of (B)(1) can be a monohydric alcohol, a polyhydric alcohol, a hydroxy aromatic compound such as a phenolic compound, and  
25 mixtures thereof. Monohydric alcohols include various hydrocarbyl alcohols such as ethanol, allyl alcohol, dodecanol, and benzyl alcohol. Polyhydric alcohols include diols such as ethylene glycol, diethylene glycol, propylene glycol, 1,2-butanediol and neopentyl glycol. Polyhydric alcohols also include glycerol, trimethylolpropane, erythritol, pentaerythritol, arabitol, mannitol and sorbitol. Preferred are polyhydric  
30 alcohols, especially trimethylolpropane and pentaerythritol.

The mixtures of amine and alcohol for the reaction product of (B)(1) can be two or more amines, two or more alcohols, or one or more amines and one or more alcohols. A preferred mixture for the reaction product of (B)(1) includes an amine and an alcohol, while a more preferred mixture includes a polyamine and a polyhydric  
35 alcohol. The mixture of amines and/or alcohols can be introduced into the reaction concurrently as a true mixture or sequentially as separate components. In a preferred



5 embodiment a polyhydric alcohol is initially introduced into the reaction and later a polyethylenepolyamine is added.

The reaction product of (B)(1) can be prepared by various well known methods. A hydrocarbyl-substituted succinic acylating agent and an amine such as a polyethylenepolyamine can be reacted to form a succinimide derivative as described  
10 in U.S. Patent Nos. 4,234,435; 5,569,644; and 6,165,235. A hydrocarbyl-substituted succinic acylating agent can be reacted with an alcohol such as a polyhydric alcohol to form a succinate ester derivative as described in U.S. Patent No. 3,522,179. A hydrocarbyl-substituted succinic acylating agent can be reacted with a mixture of amines and/or alcohols such as a mixture of a polyhydric alcohol and a polyamine to  
15 form a nitrogen-containing succinate ester derivative as described in U.S. Patent No. 4,904,401.

The component (B) can include the polyalkenylthiophosphonate ester of (B)(2). The polyalkenyl substituent of the ester of (B)(2) can have a number average molecular weight of 300 to 5000, preferably of 400 to 2000, and more preferably of  
20 500 to 1500. The polyalkenyl substituent can be derived from an olefin which is typically a polyolefin as described above for the hydrocarbyl substituent of the succinic acylating agent of the reaction product of (B)(1). The ester of (B)(2) can be prepared as described in U.S. Patent No. 5,725,611 by reacting a polyolefin with a thiophosphorylating agent at elevated temperatures to form an adduct, generally steam  
25 treating the adduct at elevated temperatures to form a thiophosphonic acid, and finally reacting the thiophosphonic acid with a polyhydric alcohol to form the ester of (B)(2). In a preferred embodiment the polyolefin is polyisobutylene, the thiophosphorylating agent is phosphorus pentasulfide, and the polyhydric alcohol is pentaerythritol.

The component (B) may also include the Mannich reaction product of (B)(3)  
30 of a hydrocarbyl-substituted phenol, an aldehyde, and an amine. The hydrocarbyl substituent of the phenol can have a number average molecular weight of 200 to 3000, preferably of 350 to 2000, and more preferably of 500 to 1500. The hydrocarbyl substituent of the phenol can be derived from an olefin and is typically derived from a polyolefin as described above for the hydrocarbyl substituent of the succinic acylating  
35 agent of the reaction product of (B)(1). The hydrocarbyl-substituted phenol can be prepared by well known methods including acid catalyzed alkylation of a phenolic

5 compound with a polyolefin as described in U.S. Patent No. 5,876,468. The phenolic compound can be phenol, an alkyl-substituted phenol, or mixtures thereof. The alkyl substituent of the alkyl-substituted phenol can have 1 to 10 carbon atoms. The alkyl-substituted phenol is preferably an ortho-alkyl substituted phenol such as o-cresol.

The aldehyde of the Mannich reaction product of (B)(3) can have 1 to 6  
10 carbon atoms and is preferably formaldehyde in one of its reagent forms such as paraformaldehyde and formalin.

The amine of the Mannich reaction product of (B)(3) can be a monoamine, polyamine, alkanolamine, any organic compound containing a reactive N-H group, or mixtures thereof. The amine contains at least one N-H group capable of undergoing  
15 the Mannich reaction. Monoamines include ammonia and primary or secondary amines having 1 to 22 carbon atoms such as butylamine and dimethylamine. Polyamines include alkylenediamines such as ethylenediamine and polyethylene-polyamines such diethylenetriamine. Alkanolamines include compounds having 1 to 22 carbon atoms, that contain at least one primary or secondary amine group, and that  
20 contain at least one hydroxy group such as ethanolamine, diethanolamine and aminoethylethanolamine.

The Mannich reaction product of (B)(3) can be prepared by methods that are well known to include the method described in U.S. Patent No. 5,876,468.

The jet fuel additive concentrate composition of the present invention can  
25 include (B)(4) mixtures thereof of subcomponents (B)(1)-(B)(3) as well as described hereinbelow (C)(7) mixtures thereof of subcomponents (C)(5)-(C)(6) and (D)(14) mixtures thereof of subcomponents (D)(8)-(D)(13). These subcomponent mixtures can include any two or more subcomponents from that component group. For example, the subcomponent mixture (B)(4) can include a subcomponent from (B)(1) and from (B)(2), and in another instance can include two different members of  
30 subcomponent (B)(1).

The component (C) can include the metal salt of (C)(5) of an oligomeric reaction product of a hydrocarbyl-substituted phenol and an aldehyde. The hydrocarbyl substituent of the hydrocarbyl-substituted phenol can have 4 to 40 carbon  
35 atoms, preferably 5 to 30 carbon atoms, and more preferably 6 to 20 carbon atoms. The hydrocarbyl substituent can be derived from an olefin such as a heptene. The



5 hydrocarbyl substituent can also be derived from a polyolefin to include homopolymers derived from a single olefin monomer and copolymers derived from a mixture of two or more different monomers. The olefin monomer can be an alpha-olefin, internal olefin or a polyene to include ethylene, propylene, isomers of butene, isomers of pentene, isomers of decene and dienes. A preferred polyolefin is a polypropylene  
10 tetramer. The olefins and polyolefins, from which the hydrocarbyl substituent can be derived, are commercially available, and the polyolefins can also be prepared by well known polymerization methods. The hydrocarbyl-substituted phenols of the metal salt of (C)(5) can be prepared by alkylating phenol with an olefin or polyolefin by very well known methods and are also commercially available. The aldehyde of the  
15 metal salt of (C)(5) can contain 1 to 6 carbon atoms and is preferably formaldehyde in a reactant form such as paraformaldehyde or formalin. The metal salt of the reaction product of (C)(5) can be prepared by several known methods. In one method the hydrocarbyl-substituted phenol and aldehyde are reacted in the presence of an acid catalyst to form the oligomer, and then the oligomer is reacted with a metal base to  
20 form the salt. In another method, as described in U.S. Patent No. 3,256,183, the hydrocarbyl-substituted phenol, aldehyde and metal base are reacted to form the metal salt of the oligomeric reaction product. The metal of the metal base includes alkali metals, alkaline earth metals, zinc, cadmium, iron, nickel, cobalt, copper, tin and mixtures thereof. The metal salt can be neutral by having up to one equivalent of  
25 metal per phenol or be basic by having greater than one equivalent of metal per phenol. In a preferred embodiment the metal salt of (C)(5) is a neutral salt that is prepared by reacting dodecylphenol, formaldehyde and hydrated lime (calcium hydroxide).

The component (C) can include the oligomeric reaction product of (C)(6) of a  
30 hydrocarbyl-substituted phenol, an aldehyde, and a carboxyl-substituted phenol. The hydrocarbyl substituent of the hydrocarbyl-substituted phenol can have 1 to 60 carbon atoms, preferably 5 to 50 carbon atoms, and more preferably 7 to 40 carbon atoms. The hydrocarbyl substituent can be derived from an olefin. The hydrocarbyl substituent is typically derived from a polyolefin which can be a homopolymer from  
35 one olefin monomer or a copolymer from a mixture of two or more olefin monomers. The olefin monomer can be an alpha-olefin, an internal olefin, or a polyene and

5 includes ethylene, propylene, butene isomers, pentene isomers, decene isomers, and  
dienes. Preferred are polypropylenes and polyisobutylenes. Methods to prepare the  
polyolefins and the hydrocarbylphenols via alkylation of phenol with olefins or  
polyolefins are well known. The aldehyde of the oligomeric reaction product of  
10 (C)(6) can have 1 to 6 carbon atoms. The aldehyde is preferably formaldehyde in one  
of its reactive forms such as formalin or paraformaldehyde. The carboxyl-substituted  
phenol of the oligomeric reaction product of (C)(6) can be a 2- or 3- or 4-  
hydroxybenzoic acid which can have hydrocarbyl substituents. Preferred is salicylic  
acid. The oligomeric reaction product of (C)(6) contains at least one hydrocarbyl-  
substituted phenolic unit and at least one carboxyl-substituted phenolic unit. The  
15 oligomeric reaction product can contain 2 to 20 phenolic units, 2 to 10 phenolic units,  
or 2 to 8 phenolic units. The oligomeric reaction product can include linear  
molecules, cyclic molecules, or mixtures thereof. In a preferred embodiment the  
oligomeric reaction product is a mixture of linear and cyclic molecules, and in a more  
preferred embodiment the mixture contains a majority of linear molecules. The  
20 oligomeric reaction product can be prepared as described in U.S. Patent No.  
6,200,936 using a basic catalyst and a solvent. Basic catalysts include alkali and  
alkaline earth metal bases and amines such as lithium hydroxide, sodium hydroxide,  
potassium hydroxide and ammonium hydroxide. A solvent can be employed in the  
preparation of the oligomeric reaction product up to 90% by weight of the reaction  
25 mixture. The mole ratio of the hydrocarbyl-substituted phenol to the carboxyl-  
substituted phenol can range from 1:0.05 to 1:19 while the mole ratio of combined  
hydrocarbyl-substituted phenol and carboxyl-substituted phenol to aldehyde can be  
1:0.5-3.

The jet fuel additive concentrate composition of the present invention can  
30 include an antioxidant, a metal deactivator, or mixtures thereof. Useful antioxidants  
include secondary aromatic amines such as a N-substituted phenylenediamines and  
ring alkylated diphenylamines and also include hindered phenolic compounds such as  
2,4-dimethyl-6-tertiary-butylphenol, 2,6-di-tertiary-butyl-4methylphenol, 2,6-di-  
tertiary-butyl-4-methoxyphenol, 2,6-di-tertiary-butylphenol, and 2,4,6-tri-tertiary-  
35 butylphenol. The metal deactivator includes Schiff bases from salicylaldehyde such as  
N,N'-bis(salicylidene)-1,2-propanediamine, N-salicylideneaniline, and N,N'-



5 bis(salicylidene)ethylenediamine and also includes certain triazole derivatives such as tolyltriazole coupled with formaldehyde to bis(2-ethylhexyl)amine. The antioxidants and metal deactivators can be prepared by well known methods and are also commercially available.

A fuel composition of the present invention comprises a jet fuel and the jet  
10 fuel additive concentrate composition of the present invention as described throughout this application. The jet fuel can include aviation turbine fuels such as JP-4, JP-5, JP-7, JP-8, Jet A, Jet-A-1 and Jet B. JP-4, JP-5, JP-7 and JP-8 are military grades of jet fuels. JP-4 is a blend of gasoline and kerosene and JP-5 is a very high flash point fuel with both fuels defined in U.S. military specification MIL-DTL-5624. JP-7 and JP-8  
15 are highly refined kerosenes with JP-8 defined by U.S. military specification MIL-DTL-83133. JP-4, JP-5 and JP-8 are required for safety and performance reasons to contain a corrosion inhibitor, an icing inhibitor and a static dissipater. Jet A, Jet A-1 and Jet B are commercial grades of jet fuels as defined in ASTM standard specification D1655. Jet A and Jet A-1 are relatively high flash point kerosene  
20 distillates with Jet A-1 being equivalent to JP-8. Jet B is a relatively wide boiling range volatile distillate that is equivalent to JP-4.

The jet fuel additive concentrate composition and fuel composition of the present invention, as described throughout this application, are prepared by admixing the components at or near ambient temperature until the composition is homogeneous.  
25 Jet fuel additives including antioxidants, metal deactivators, corrosion inhibitors, icing inhibitors and static dissipaters can be added directly to a jet fuel or can be introduced to a jet fuel as part of a jet fuel additive concentrate composition.

A method of the present invention to improve the thermal stability of a jet fuel comprises adding to the jet fuel a thermal-stability improving amount of a jet fuel  
30 additive concentrate composition as described throughout this application. The jet fuel includes those fuels described hereinabove. Thermal-stability improving amounts of the jet fuel additive concentrate composition and its components are described hereinbelow. In addition to the method to improve the thermal stability of a jet fuel, a method to reduce deposits in a fuel circulation system and combustion  
35 system of a jet engine comprises operating the jet engine with a fuel composition of the present invention. The fuel composition will normally contain a thermal-stability

5 improving amount of the jet fuel additive concentrate composition of the present invention as described throughout this application.

The jet fuel additive concentrate composition, in addition to components (A), (B) and (C), can further comprise (D) a cold-flow improving composition selected from the group consisting of (8) an esterified copolymer of maleic anhydride, styrene  
10 and optionally an alkyl methacrylate; (9) a copolymer of a dialkyl fumarate, a vinyl ester of a carboxylic acid and optionally a vinyl alkyl ether; (10) a methacrylate polymer prepared from a mixture of alkyl methacrylate monomers; (11) a copolymer of an olefin selected from the group consisting of olefins having 2 to 12 carbon atoms and mixtures thereof, and a vinyl ester of a carboxylic acid; (12) a polymer prepared  
15 from the reaction of an alkylphenol and formaldehyde wherein the alkyl substituent of the alkylphenol has 14 to 60 carbon atoms; (13) a reaction product of a hydrocarbyl substituted acylating agent and an amine selected from the group consisting of an alkanolamine and a polyamine wherein the hydrocarbyl substituent of (D)(13) has 8 to 40 carbon atoms; and (14) mixtures thereof wherein each of the compositions for  
20 component (D) is present in the concentrate composition at 1-70 weight %.

The esterified copolymer of (D)(8), as described in U.S. Patent No. 5,707,943, can be prepared from the monomers maleic anhydride, styrene and optionally an alkyl acrylate or methacrylate such as methyl methacrylate. The copolymer prior to esterification typically has a molecular weight expressed in terms of a reduced  
25 specific viscosity or RSV value ranging from 0.05 to 2, preferably from 0.1 to 0.75, and more preferably from 0.12 to 0.4. The copolymer is normally esterified with a mixture of lower and higher molecular weight alcohols having respectively 3 to 5 carbon atoms and 8 to 24 carbon atoms. The esterified copolymer will typically have some unesterified carboxylic groups which can be reacted with ammonia, a  
30 monoamine or a polyamine such as 4-(3-aminopropyl)morpholine.

The copolymer of (D)(9) is derived from a dialkyl fumarate monomer, a monomer that is a vinyl ester of a carboxylic acid or an alkyl acrylate or methacrylate, and optionally a vinyl alkyl ether monomer. The dialkyl fumarate can be derived from C<sub>6</sub> to C<sub>30</sub> alcohols, preferably C<sub>8</sub> to C<sub>26</sub> alcohols which can be a single alcohol  
35 such decyl alcohol, but is typically a mixture of two or more alcohols. The carboxylic portion of the vinyl carboxylate ester or the alkyl portion of the acrylate or



- 5 methacrylate ester can have 1 to 10 carbon atoms, preferably 2-6 carbon atoms. The alkyl portion of the vinyl alkyl ether can have about 1 to 10 carbon atoms. The copolymer of (D)(9) can be derived from a dialkyl fumarate and vinyl acetate as described in U.S. Patent No. 6,017,370 where the copolymer can have a number average molecular weight of 2,000 to 100,000 with 10,000 to 45,000 being preferable.
- 10 The copolymer of (D)(9) can be derived from a dialkyl fumarate, vinyl acetate and vinyl ethyl ether as described in U.S. Patent No. 3,250,715 where the copolymer can have a specific viscosity of 0.09 to 0.8.

The methacrylate polymer of (D)(10) can be derived from a hydrocarbyl methacrylate monomer or preferably a mixture of two or more hydrocarbyl methacrylate monomers. The hydrocarbyl group of the methacrylate monomer or monomers is usually a linear or branched alkyl group having about 4 to 30 carbon atoms, preferably having about 6 to 24 carbon atoms. Methacrylate monomers are available commercially or can be prepared by well known esterification methods. The methacrylate polymer of the present invention can also contain a nitrogen containing monomer to include a 2- and 4-vinylpyridine, nitrogen-containing alkyl methacrylates and acrylates such as N,N-dimethylaminopropyl methacrylate, and acrylamides. Methacrylate polymers can be prepared by well known polymerization methods as described in European Publication No. 626442A1 resulting in polymers having a weight average molecular weight of about 10,000 to 1,000,000, and preferably 50,000 to 300,000.

The copolymer of (D)(11) can be derived from an olefin selected from the group consisting of olefins having 2 to 12 carbon atoms and mixtures thereof, and a vinyl ester of a carboxylic acid or an alkyl ester of an alkenoic acid. Olefins include ethylene, propylene, butene isomers, and mixtures thereof. Vinyl carboxylate esters include vinyl acetate and vinyl propionate. Alkyl alkenoate esters include alkyl acrylate and methacrylate esters. The copolymer of (D)(11) can contain an additional monomer to include vinyl alkyl ethers and vinyl ketones. A preferred copolymer of (D)(11) is an olefin vinyl carboxylate copolymer such as an ethylene vinyl acetate copolymer. The ethylene vinyl acetate copolymer can have a number average molecular weight of about 1,000 to 10,000, preferably about 1,500 to 5,000, and more preferably about 1,800 to 4,000. The ethylene vinyl acetate copolymer can have a

5 weight ratio of ethylene to vinyl acetate of about 0.25-3:1, and preferably of about 0.5-2:1. Ethylene vinyl acetate copolymers can be prepared by well known polymerization methods and are also available commercially.

The polymer of (D)(12) can be derived from a hydrocarbyl substituted, hydroxy containing aromatic compound and an aldehyde. The hydroxy containing  
10 aromatic compound is preferably phenol and the hydrocarbyl substituent is typically an alkyl substituent. The alkyl substituent can have about 8 to 80 carbon atoms, preferably 12 to 70 carbon atoms, and more preferably 14 to 60 carbon atoms. Alkyl substituents having 16 to 18 carbon atoms, 24 to 28 carbon atoms, or at least 30 carbon atoms are useful in the present invention. The alkyl substituent can be derived  
15 from an olefin or a polyolefin. The polyolefin can be a homopolymer derived from an olefin monomer or a copolymer derived from a mixture of two or more olefin monomers. The olefin monomers typically have 2 to about 10 carbon atoms such as ethylene, propylene and isomers of butene. Alkylphenols are prepared by well known procedures such as acid catalyzed alkylation of phenol with an olefin or polyolefin as  
20 described in U.S. Patent No. 5,707,946. The aldehyde can have about 1 to 10 carbon atoms and includes formaldehyde, acetaldehyde, propionaldehyde and glyoxylic acid. Formaldehyde is preferred in one of its reagent forms such as formalin or paraformaldehyde. The polymer of (D)(12) can be prepared by well known methods to include a base or acid catalyzed condensation reaction. A preferred method of  
25 condensation is an acid condensation as described in U.S. Patent No. 5,707,946. The mole ratio of the alkylphenol to aldehyde can be about 1:0.5-2, preferably about 1:1-1.2. The number average molecular weight of the polymer of (D)(12) is about 1,000 to 35,000, and preferably about 2,500 to 8,000.

The reaction product of (D)(13) can be derived from a hydrocarbyl substituted  
30 acylating agent and an alkanolamine where the acylating agent is an alkenylsuccinic acylating agent. The hydrocarbyl or alkenyl substituent can have about 8 to 40 carbon atoms, preferably 12 to 36 carbon atoms. The alkenyl substituent can be derived from an olefin or polyolefin, preferably a polyolefin. The polyolefin can be branched or linear. The polyolefin can be derived typically from ethylene although other olefin  
35 monomers can be present. The polyolefin can be an alpha-olefin or internalized olefin, but is typically an alpha-olefin. The polyolefin can be a single polyolefin or a



5 mixture of two or more polyolefins which on the average has about 8 to 40 carbon atoms. The polyolefins and mixtures of polyolefins are available commercially. Methods to prepare an alkenylsuccinic acylating agent are well known and include reacting a polyolefin or mixture of polyolefins with maleic anhydride or a reactive equivalent thereof at a temperature of about 160-240°C as described in U.S. Patent  
10 No. 6,017,370. The alkanolamine used to prepare the reaction product of (D)(13) can contain one or more amino groups, which can be primary or secondary or tertiary, and one or more hydroxy groups. Examples of useful alkanolamines are ethanolamine, diethanolamine, triethanolamine, N-methylethanolamine, N,N-dimethylethanolamine, N-ethylethanolamine, N,N-diethylethanolamine, and 2-(2-aminoethylamino)ethanol.  
15 The mole ratio of the alkenylsuccinic acylating agent to the alkanolamine can be about 1:0.5-2, preferably about 1:1-1.2. Methods to prepare the reaction product of (D)(13) are well known and include the procedures described in U.S. Patent No. 6,017,370. The reaction product of (D)(13) can also be derived from a hydrocarbyl substituted acylating agent and a polyamine where the hydrocarbyl substituent is  
20 derived from an olefin or polyolefin having 8-40 carbon atoms. The polyamine can include alkylenediamines and polyalkylenepolyamines. The (D)(13) reaction product of a hydrocarbyl substituted acylating agent and polyamine can include products such as those commercially available under the trademark Leunasol from Leuna Werke AG including Leunasol WA3020, a low molecular weight polymer prepared from maleic  
25 anhydride, C<sub>14</sub>-C<sub>18</sub> alkenes and N-tallow dipropylenetriamine.

The cold-flow improving component (D) of the present invention as described hereinabove when added to or mixed with a jet fuel improves the low temperature properties of the jet fuel. A jet fuel composition of the present invention then comprises a mixture of a jet fuel and one or more cold-flow improving compositions  
30 of component (D) capable of improving the low temperature properties of the jet fuel wherein component (D) is selected from the group consisting of (D)(8) through (D)(14) as described hereinabove. The low temperature properties of a jet fuel include the freezing point and also filterability and flow. The freezing point of a jet fuel or jet fuel composition can be measured by ASTM test methods D 2386, D 4305,  
35 D 5901 or D 5972. The filterability and flow of a jet fuel or jet fuel composition can be measured by a Jet Fuel Filterability Test that simulates low temperature fuel flow

5 in a wing tank by using the same ratio of fuel volume to drain hole area that is present in the wing tank. The amount of the cold-flow improving component (D) added to a jet fuel can vary, but generally will be an amount that improves the low temperature properties of the jet fuel.

10 The concentrate and fuel compositions of the present invention can contain solvents, metal deactivators, antioxidants and the components (B), (C) and (D) as described above at levels that provide improved performance. The compositions for components (B), (C) and (D) will normally be present at levels that enhance cold flow and/or thermal stability performance of a jet fuel. The solvent can be present in a concentrate composition at about 20-80 weight %, preferably at about 30-70 weight  
15 %. Each of the compositions for components (B), (C) and (D) can be present in the concentrate composition at about 1-70 weight %, preferably at about 2-50 weight %. The concentrate composition can be present in a fuel composition at about 10-15,000 ppm by weight, preferably at about 50-10,000 ppm by weight, and more preferably at about 100-1,500 ppm by weight. Each of the compositions for components (B) and  
20 (C) can be present in the fuel composition at about 1-1,000 ppm by weight, preferably at about 2-600 ppm by weight, and more preferably at about 3-400 ppm by weight. Each of the compositions for component (D) can be present in the fuel composition at about 1-5,000 ppm by weight, preferably at about 10-3,000 ppm by weight, and more preferably at about 50-1,000 ppm by weight.

25 The following examples demonstrate the improvement in the thermal stability of a jet fuel containing a jet fuel additive concentrate composition of the present invention. Combinations of component (B) and component (C) compositions give an increase in thermal stability performance. The addition of a cold-flow improving composition of component (D) to a combination of component (B) and component  
30 (C) compositions results in an unexpected synergistic improvement in thermal stability performance.

Tables I and II contain results from the Isothermal Corrosion Oxidation Test (ICOT) which evaluates oxidative and thermal stability of a jet fuel sample. The sample in a glass tube is held at 180°C for 5 hours while air is bubbled through the  
35 sample at a rate of 1.3 liters per hour. Test results are reported as milligrams of deposits formed on the glass tube per liter of sample with fewer deposits representing



- 5 a more oxidatively and thermally stable fuel composition. Levels of components (B), (C) and (D) used in the jet fuel samples for ICOT evaluation are given in ppm by weight units.

Table I

Example	Component (B)	Component (C)	ICOT deposits, mg/L
1 (untreated fuel)			176
2 (comparative)	71 ppm <sup>1</sup>		22
3	55 ppm <sup>1</sup>	13 ppm <sup>2</sup>	10
4 (comparative)	70 ppm <sup>3</sup>		79
5	54 ppm <sup>3</sup>	13 ppm <sup>2</sup>	62

10 <sup>1</sup> Component (B) is the product of polyisobutenylsuccinic anhydride from 1000 molecular weight polyisobutene, pentaerythritol and polyethylenepolyamines reacted in a ratio of 1 carbonyl:1.8 hydroxyl:0.26 nitrogen.

<sup>2</sup> Component (C) is the calcium salt of formaldehyde coupled heptylphenol from a reaction ratio of 1 phenol:1.4 aldehyde:0.8 metal equivalents as hydrated lime.

15 <sup>3</sup> Component (B) is the product of polyisobutenylsuccinic anhydride from 1000 molecular weight polyisobutene and a condensed polyamine reacted in a ratio of 1 carbonyl:1.55 nitrogen where the condensed polyamine is the phosphoric acid catalyzed condensation product of polyethylenepolyamine bottoms and 40% trishydroxymethylaminomethane in an aqueous solution reacted in a weight ratio of respectively 1:0.61.

20

Table II

Example	Components (B) + (C)	Component (D)	ICOT deposits, mg/L
1 (untreated fuel)			690
2 (comparative)	17 ppm <sup>1</sup>		246
3 (comparative)		125 ppm <sup>2</sup>	566
4 (comparative)		132 ppm <sup>3</sup>	704
5 (comparative)		250 ppm <sup>4</sup>	339
6	17 ppm <sup>1</sup>	125 ppm <sup>2</sup>	8
7	17 ppm <sup>1</sup>	132 ppm <sup>3</sup>	44
8	17 ppm <sup>1</sup>	250 ppm <sup>4</sup>	11

- 5     <sup>1</sup>     Components (B) and (C) are 14 ppm of the component (B) described in footnote 1 of Table 1 and 3 ppm of the component (C) described in footnote 2 of Table I.
- 10     <sup>2</sup>     Component (D) is the p-toluenesulfonic acid catalyzed condensation product of a C<sub>24</sub>-C<sub>28</sub> alkylphenol and 91% paraformaldehyde reacted in a weight ratio of respectively 12.5:1.
- 15     <sup>3</sup>     Component (D) is the product of a C<sub>18</sub>-C<sub>30</sub> alkenylsuccinic anhydride and diethanolamine reacted in a weight ratio of respectively 10:2.44.
- 15     <sup>4</sup>     Component (D) is an ethylene vinyl acetate copolymer containing about 35.5% by weight of the vinyl acetate monomer and having a number average molecular weight of about 2200.

Each of the documents cited in this Detailed Description is incorporated herein by reference. With the exception of the examples, all numerical quantities used to describe this invention are understood to be modified by the word "about". Unless indicated otherwise quantities used for chemical compositions throughout this application are understood to be on an active chemical basis and not to include any diluent which may be present in these compositions.



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What is claimed is:

1. A jet fuel additive concentrate composition, comprising:
  - (A) a solvent suitable for use in a jet fuel;
  - 10 (B) a composition selected from the group consisting of (1) a reaction product of a hydrocarbyl-substituted succinic acylating agent and a mixture of a polyamine and a polyhydric alcohol or an acid catalyzed condensation product of a polyamine and a polyhydroxy-containing compound wherein the hydrocarbyl substituent of (B)(1) has a number average molecular weight of 600 to 3,000; (2) a
  - 15 polyalkenylthiophosphate ester wherein the polyalkenyl substituent of (B)(2) has a number average molecular weight of 300 to 5,000; and (4) mixtures thereof; and
  - (C) a composition selected from the group consisting of (5) a metal salt of an oligomeric reaction product of a hydrocarbyl-substituted phenol and an aldehyde; (6) an oligomeric reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and
  - 20 a carboxyl-substituted phenol; and (7) mixtures thereof wherein the solvent is present in the concentrate composition at 20-80 weight %, and each of the compositions for components (B) and (C) is present in the concentrate composition at 1-70 weight %.
2. The concentrate composition of claim 1 wherein the solvent comprises
- 25 xylenes, paraffinic naphtha, aromatic naphtha, or mixtures thereof.
3. The concentrate composition of claim 1 wherein the hydrocarbyl substituent of the acylating agent of (B)(1) is derived from a polyisobutene having a number average molecular weight of 700 to 1500.
- 30 4. The concentrate composition of claim 1 wherein the polyamine of the mixture of (B)(1) is a polyethylenepolyamine and the polyethylenepolyamine is introduced into the reaction after the polyhydric alcohol.
- 35 5. The concentrate composition of claim 1 wherein the acid catalyzed condensation product of (B)(1) is prepared from the reaction of polyethylenepolyamine bottoms and tris(hydroxymethyl)aminomethane.

- 5 6. The concentrate composition of claim 1 wherein the polyalkenylthiophosphonate ester of (B)(2) is a pentaerythritol ester of a polyisobutenylthiophosphonic acid.
7. The concentrate composition of claim 1 wherein the metal salt of the  
10 oligomeric reaction product of (C)(5) is the reaction product of an alkylphenol, formaldehyde, and an inorganic alkaline earth metal base wherein the alkyl substituent of the alkylphenol has 6 to 20 carbon atoms.
8. The concentrate composition of claim 1 wherein the oligomeric reaction  
15 product of (C)(6) is prepared from the reaction of an alkylphenol, formaldehyde, and salicylic acid wherein the alkyl substituent of the alkylphenol has 7 to 40 carbon atoms.
9. The concentrate composition of claim 1, further comprising:  
20 an antioxidant, a metal deactivator, or mixtures thereof.
10. A fuel composition, comprising:  
a jet fuel; and  
the concentrate composition of claim 1 wherein each of the compositions for  
25 components (B) and (C) is present in the fuel composition at 1-1,000 ppm by weight.
11. The fuel composition of claim 10 wherein the jet fuel is selected from the group consisting of JP-4, JP-5, JP-7, JP-8, Jet A, Jet A-1, and Jet B.
- 30 12. A method to improve the thermal stability of a jet fuel, comprising:  
adding to the jet fuel a thermal-stability improving amount of the concentrate composition of claim 1.
13. A method to reduce deposits in a fuel circulation system and combustion  
35 system of a jet engine, comprising:  
operating the jet engine with the fuel composition of claim 10.
14. The concentrate composition of claim 1, further comprising:



5 (D) a cold-flow improving composition selected from the group consisting of  
(8) an esterified copolymer of maleic anhydride, styrene, and optionally an alkyl  
methacrylate; (9) a copolymer of a dialkyl fumarate, a vinyl ester of a carboxylic acid,  
and optionally a vinyl alkyl ether; (10) a methacrylate polymer prepared from a  
mixture of alkyl methacrylate monomers; (11) a copolymer of an olefin selected from  
10 the group consisting of olefins having 2 to 12 carbon atoms and mixtures thereof, and  
a vinyl ester of a carboxylic acid; (12) a polymer prepared from the reaction of an  
alkylphenol and formaldehyde wherein the alkyl substituent of the alkylphenol has 14  
to 60 carbon atoms; (13) a reaction product of a hydrocarbyl substituted acylating  
agent and an amine selected from the group consisting of an alkanolamine and a  
15 polyamine wherein the hydrocarbyl substituent of (D)(13) has 8 to 40 carbon atoms;  
and (14) mixtures thereof wherein each of the compositions for component (D) is  
present in the concentrate composition at 1-70 weight %.

15. The concentrate composition of claim 14 wherein the esterified copolymer of  
20 (D)(8) is further reacted with an amine.

16. The concentrate composition of claim 14 wherein the copolymer of (D)(11) is  
a copolymer of ethylene and vinyl acetate.

25 17. The concentrate composition of claim 14 wherein the polymer of (D)(12) is  
prepared from an alkylphenol wherein the alkyl group has 24 to 28 carbon atoms.

18. The concentrate composition of claim 14 wherein the polymer of (D)(12) is  
prepared from an alkylphenol wherein the alkyl group has at least 30 carbon atoms.

30 19. The concentrate composition of claim 14 wherein the reaction product of  
(D)(13) is the reaction product of an alkenylsuccinic acylating agent and  
alkanolamine wherein the alkenyl group has 12 to 36 carbon atoms and the  
alkanolamine is dimethylethanolamine or diethanolamine.

35 20. The concentrate composition of claim 14, further comprising:  
an antioxidant, a metal deactivator, or mixtures thereof.

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5 21. The fuel composition of claim 10 wherein the concentrate composition further  
comprises (D) a cold-flow improving composition selected from the group consisting  
of (8) an esterified copolymer of maleic anhydride, styrene, and optionally an alkyl  
methacrylate; (9) a copolymer of dialkyl fumarate, a vinyl ester of a carboxylic acid,  
10 and optionally a vinyl alkyl ether; (10) a methacrylate polymer prepared from a  
mixture of alkyl methacrylate monomers; (11) a copolymer of an olefin selected from  
the group consisting of olefins having 2 to 12 carbon atoms and mixtures thereof, and  
a vinyl ester of a carboxylic acid; (12) a polymer prepared from the reaction of an  
alkylphenol and formaldehyde wherein the alkyl substituent of the alkylphenol has 14  
to 60 carbon atoms; (13) a reaction product of a hydrocarbyl substituted acylating  
15 agent and an amine selected from the group consisting of an alkanolamine and a  
polyamine wherein the hydrocarbyl substituent of (D)(13) has 8 to 40 carbon atoms;  
and (14) mixtures thereof wherein each of the compositions for component (D) is  
present in the concentrate composition at 1-70 weight % and each of the compositions  
is present in the fuel composition for component (D) at 1-5,000 ppm by weight.

20

22. The fuel composition of claim 21 wherein the jet fuel is selected from the  
group consisting of JP-4, JP-5, JP-7, JP-8, Jet A, Jet A-1, and Jet B.

23. The method of claim 12 wherein the concentrate composition further  
25 comprises (D) a cold-flow improving composition selected from the group consisting  
of (8) an esterified copolymer of maleic anhydride, styrene, and optionally an alkyl  
methacrylate; (9) a copolymer of dialkyl fumarate, a vinyl ester of a carboxylic acid,  
and optionally a vinyl alkyl ether; (10) a methacrylate polymer prepared from a  
mixture of alkyl methacrylate monomers; (11) a copolymer of an olefin selected from  
30 the group consisting of olefins having 2 to 12 carbon atoms and mixtures thereof, and  
a vinyl ester of a carboxylic acid; (12) a polymer prepared from the reaction of an  
alkylphenol and formaldehyde wherein the alkyl substituent of the alkylphenol has 14  
to 60 carbon atoms; (13) a reaction product of a hydrocarbyl substituted acylating  
agent and an amine selected from the group consisting of an alkanolamine and a  
35 polyamine wherein the hydrocarbyl substituent of (D)(13) has 8 to 40 carbon atoms;  
and (14) mixtures thereof wherein each of the compositions for component (D) is  
present in the concentrate composition at 1-70 weight %.



- 5 24. The method of claim 13 wherein the concentrate composition of the fuel  
composition further comprises (D) a cold-flow improving composition selected from  
the group consisting of (8) an esterified copolymer of maleic anhydride, styrene, and  
optionally an alkyl methacrylate; (9) a copolymer of dialkyl fumarate, a vinyl ester of  
a carboxylic acid, and optionally a vinyl alkyl ether; (10) a methacrylate polymer  
10 prepared from a mixture of alkyl methacrylate monomers; (11) a copolymer of an  
olefin selected from the group consisting of olefins having 2 to 12 carbon atoms and  
mixtures thereof, and a vinyl ester of a carboxylic acid; (12) a polymer prepared from  
the reaction of an alkylphenol and formaldehyde wherein the alkyl substituent of the  
alkylphenol has 14 to 60 carbon atoms; (13) a reaction product of a hydrocarbyl  
15 substituted acylating agent and an amine selected from the group consisting of an  
alkanolamine and a polyamine wherein the hydrocarbyl substituent of (D)(13) has 8 to  
40 carbon atoms; and (14) mixtures thereof wherein each of the compositions for  
component (D) is present in the concentrate composition at 1-70 weight %, and each  
of the compositions is present in the fuel composition for component (D) at 1-5,000  
20 ppm by weight.