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(54) **CONDUCTIVITY IMPROVING COMBINATION OF CERIUM OXIDE AND DETERGENTS FOR DIESEL FUELS**

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(57) **ABSTRACT**

The disclosure provides conductivity improving concentrates and methods for improving conductivity and reducing risks associated with static discharge in middle distillate fuel composition compositions, particularly diesel fuels. The conductivity improvement is provided with the combination of cerium oxide nanoparticles and dispersant/detergent and shows aged conductivity comparable to or higher than that obtained with conventional antistatic agents.

CONDUCTIVITY IMPROVING COMBINATION OF CERIUM OXIDE AND DETERGENTS FOR DIESEL FUELS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. application Ser. No. 11/533,200 filed on Sep. 19, 2006 and entitled Diesel Fuel Additives Containing Cerium or Manganese and Detergents.

FIELD OF THE DISCLOSURE

[0002] The disclosure relates to diesel fuel additives to impart improved combustion, and improved fuel stability to the finished diesel fuel. The disclosure also relates to compositions and methods for improving the conductivity of middle distillate fuel compositions, particularly diesel fuels and most particularly low sulfur and ultra-low sulfur diesel fuels.

BACKGROUND OF THE DISCLOSURE

[0003] Cerium oxide nanoparticles have been used in diesel fuel applications as a catalyst for converters in the elimination of toxic exhaust emission gases. Cerium oxide has also shown utility in reducing the emission from diesel engines of particulate emissions. Envirox™ Fuel Borne Catalyst is a diesel fuel combustion improver which reduces fuel consumption and also reduces harmful exhaust emissions.

[0004] Certain organometallic compounds have been found effective as combustion improvers for distillate fuels such as home heating oils and the like. For example, U.S. Pat. No. 3,112,789 describes the use of cyclopentadienyl manganese tricarbonyls for this purpose, and the compound methylcyclopentadienyl manganese tricarbonyl (MMT) has been sold in the form of a solution in a hydrocarbon diluent as a combustion improver for distillate fuels of this type. Bis (cyclopentadienyl) iron has also been promoted and sold as a combustion improver for use in such fuels.

[0005] U.S. Pat. Nos. 3,883,320 and 3,891,401 teach the addition of salts of a transition metal, such as manganese, and an alkaline earth metal, such as calcium, to jet fuels for reducing deposits and smoke. These patents require a manganese/calcium weight ratio of about 5/1 and the combined amounts of metals within the range of from 200 to 600 ppm (200 to 500 ppm in the '401 patent).

[0006] However, difficulties can arise in the formulating of diesel fuels with certain additive packages resulting in haze, precipitates, insolubilities, inadequate fuel economy, and insufficient smoke reduction. A need has arisen for a fuel-soluble additive composition for hydrocarbonaceous fuels that is not only capable of reducing the amount of soot, smoke and/or carbonaceous products produced on combustion of the fuel but that is capable of improving solubility in the fuel, and enhancing fuel economy resulting from the combustion of the fuel. In fulfilling this need, it is also important to provide an additive which prevents or at least inhibits the deposition of sludge on critical engine or burner parts or surfaces and which provides fuel compositions having satisfactory physical properties such as thermal stability and storage stability. It is also highly desirable to provide an additive composition which is capable of reducing or inhibiting the amount of noxious emissions (e.g., carbon monoxide, unburned hydrocarbons, polyaromatic hydrocarbons, and/or particulates) formed when using the fuels in an engine or in a burner or like combustion apparatus. The provision of additive compositions capable of decreasing fuel consumption is also a most desirable objective. A need therefore exists for an improved diesel fuel additive and diesel fuel additive package that provides improved combustion, improved solubility of the organometallic fuel additives, reduced haze, improved smoke reduction, and enhanced fuel economy.

[0007] Certain middle distillate fuel compositions, particularly diesel fuels, are capable of generating static electricity, particularly when moving rapidly, such as when the fuel is being dispensed into a tanker or other bulk container or vessel. While diesel fuels are not very volatile, the tankers used to transport diesel fuels are also used to transport gasoline, kerosene and other more volatile and flammable liquids. Even after the more volatile fuel is dispensed from the tanker, the vapors may still be present and pose a risk of fire or explosion from a spark generated by the discharge of static electricity from the fuel composition.

[0008] These risks have become more acute in recent years with the increased popularity and use of low sulfur fuels and even more acute in recent months with the introduction of ultra-low sulfur diesel fuels. The process used to remove the sulfur from the fuels also decreases the concentration of other polar compounds in the fuel, which in turn reduces the ability of the fuel to dissipate a static charge.

[0009] To mitigate the risks of fire or explosion with low and ultra-low sulfur fuels, it has become common to add a conductivity improver to the fuel at or prior to the point of dispensing the fuel into a bulk container. The conductivity improver, as the name suggests, improves the conductivity of the fuel, thus permitting any static charge built up during high volume transport of the fuel to safely dissipate without generating a spark. Conductivity improvers are also known as antistatic agents.

[0010] The most common type of conductivity improver or antistatic agent used in fuels, particularly diesel fuels, has been the Stadis® brand of antistatic agents sold by Innospec Fuel Specialties, LLC, Newark, Del. However, the Stadis® brand of antistatic agents contains sulfur. Adding the Stadis® antistatic agents to the diesel fuel thus reduces certain of the benefits of using an ultra-low sulfur fuel. In addition, these antistatic agents are quite expensive.

[0011] Moreover, sulfur-containing antistatic agents present another problem when used with additive concentrates or fuels that contain basic nitrogen. Specifically, Applicants have observed that the conductivity improvement delivered by the traditional antistatic agent dissipates very rapidly when used in additive concentrates or fuel mixtures containing basic nitrogen. This is disadvantageous because it prevents pre-blending of these antistatic agents into additive concentrates that contain basic nitrogen. Many components of a typically fuel additive concentrate include nitrogen-containing compounds, such as dispersants, detergents, cetane number improvers and the like. As a result, it is often necessary to add the sulfur-containing antistatic agents separately from the other components of the additive concentrate. Thus, these types of antistatic agents must be kept in a separate tank at the depot and added separately to the fuel. Accordingly, these types of antistatic agent, apart from their inherent additional cost, require additional costs and complexity in terms of storage, handling and dispensing.

[0012] Therefore, there is a need for compositions and methods to address the build-up and discharge of static electricity in middle distillate fuel compositions.

SUMMARY OF THE EMBODIMENTS

[0013] An embodiment presented herein provides a diesel fuel additive package containing a source of cerium, such as cerium oxide particles or nanoparticles, and a diesel fuel detergent.

[0014] In one embodiment, the diesel fuel additive package contains cerium oxide nanoparticles, a cetane number-improving agent, diesel fuel detergent and a demulsifier. More particularly, another embodiment can contain cerium oxide particles or nanoparticles, a diesel fuel detergent/dispersant containing an alkylated (HR-PIB) succinimide polyamine and cetane number improver (eg. 2-ethyl hexyl nitrate), a demulsifier and may also contain a metal de-activator.

[0015] In one embodiment, the additive package containing cerium oxide particles or nanoparticles can be used to treat diesel fuel at a treat rate of from about 1 to about 200 ppm in the diesel fuel. Higher and lower levels of cerium oxide will be desirable for certain applications.

[0016] The diesel fuel additive package of the present disclosure can also contain mixed metal combustion improvers, such as cerium/manganese and cerium/manganese/iron compounds, alloys or mixtures. One embodiment herein employs alloys of two or more metals as, or comprising, nanoparticles for improved solubility or dispersibility in the fuel.

[0017] Another embodiment herein provides a diesel fuel containing the cerium oxide nanoparticles, cetane improver and a detergent, and a low-phosphorus demulsifier.

[0018] In another embodiment herein is presented a method of improving the efficiency of a diesel fuel for an internal combustion engine which comprises adding to the fuel prior to the introduction of the fuel to a vehicle or other apparatus comprising an internal combustion engine a diesel fuel additive package comprising cerium oxide nanoparticles, a detergent and a demulsifier.

[0019] Other embodiments herein include methods for improving the efficiency of a diesel fuel (fuel economy), a method for improving diesel fuel stability, a method for reducing smoke from combustion in a diesel engine, a method for improving the solubility of an organometallic fuel additive in a diesel fuel, a method for reducing the haze in a diesel fuel having diesel fuel additives, a method for foam reduction in a diesel fuel, and a method for reducing filter blockage in a diesel fuel filter.

[0020] In other embodiment, the disclosure provides an additive concentrate for a middle distillate fuel, said concentrate comprising an antistatic agent which antistatic agent comprises, in combination, cerium oxide particles and a dispersant/detergent and a fuel containing the combination of cerium oxide particles and a dispersant/detergent as an antistatic agent.

[0021] In yet other embodiments, the disclosure provides a method of dispensing a middle distillate fuel comprising the steps of adding to the fuel an antistatic agent comprising, in combination, cerium oxide particles and a dispersant/detergent.

[0022] In another embodiment, the disclosure provides a method of reducing the risk of ignition or explosion from static discharge, comprising the steps of providing a middle distillate fuel, adding a dispersant/detergent in combination with cerium oxide particles to improve the conductivity of the fuel and thus reduce the risk of static discharge.

[0023] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present disclosure, as claimed.

DETAILED DESCRIPTION OF EMBODIMENTS

[0024] The present disclosure provides in one embodiment a diesel fuel additive package comprising cerium oxide particles or nanoparticles that are soluble or dispersible in diesel fuel. More importantly, the diesel fuel additive package contains in one embodiment a demulsifier compound to reduce or eliminate the foaming and/or emulsion problems often observed in the pumping, distribution, tank-filling and use of additized diesel fuels.

[0025] In one embodiment, the demulsifier employed in the present diesel fuel additive has a phosphorus level of greater than 30 mg/kg of demulsifier. However, it has been presently discovered that by reducing the phosphorus content, whether deliberately present or present as a contaminant, of the demulsifier in the diesel fuel additive, the stability of the fuel additive composition and of the resulting fuel is greatly enhanced and a significant reduction in haze is obtained. Thus, a level of phosphorus in the demulsifier of up to about 30 mg/kg can be used, or a phosphorus level of about 24 mg/kg has been employed, in another example about 8 mg/kg of phosphorus was employed, and in yet another formulation about 0.12 mg/kg phosphorus level was employed in the diesel fuel demulsifier. As the phosphorus level was reduced, a surprising and unexpected improvement in haze reduction and fuel stability was attained.

[0026] Demulsifiers (or dehazers) herein can be any of the commercially available materials such as but not limited to alkoxylated phenol formaldehyde polymers, such as those commercially available as “NALCO” (Trade Mark) 7007 (ex Nalco), and “TOLAD” (Trade Mark) 2683 (ex Petrolite), alkylated phenols and resins derived therefrom, oxylated alkylphenolic resin, and formaldehyde polymer with 4-(1,1-dimethylethyl)phenol, methyloxirane and oxirane, ethoxylated EO/PO resin, polyglycol ester, ethylene oxide resin.

[0027] Therefore, there is presented herein a diesel fuel additive package containing cerium oxide nanoparticles generally having a size not exceeding one micron and in one embodiment not exceeding 300 nm, for example 1 to 300 nm, such as from 1 to 150 nm, in particular 1 to 50 nm, and especially 1 to 20 nm. This diesel fuel additive package can also contain at least one diesel fuel detergent/dispersant selected from the group consisting of succinimides, Mannich bases, amides, amines, and polyetheramines.

[0028] In addition, the diesel fuel additive package can contain a demulsifier with reduced phosphorus levels of, for example, up to about 24 mg/kg, or about 8 mg/kg to about 24 mg/kg, or from about 0.1 mg/kg to about 8 mg/kg. In this manner is achieved a diesel fuel additive package able to impart to the diesel fuel superior haze reduction, improved additive solubility, increased fuel stability, smoke reduction, combustion improvement, and enhanced fuel economy.

[0029] Another benefit of the present disclosure is the improvement in the performance of the demulsifier in its intended performance in the fuel additive and in the finished fuel. Emulsions tend to form in fuels having detergents/dispersants, hence the need for the demulsifier. Any reaction which deactivates or reacts with the demulsifier reduces the demulsification efficacy, leading to more emulsification. In this manner is provided a method to improve the demulsification of a fuel additive comprising adding to the fuel additive the cerium oxide nanoparticles, a detergent and a demulsifier, wherein the demulsifier has less than about 30 mg/kg phosphorus. In another embodiment, the demulsifier has up to about 24 mg/kg, or in a separate example about 8 mg/kg to about 24 mg/kg, or in yet another example from about 0.1 mg/kg to about 8 mg/kg of phosphorus.

[0030] The amounts of cerium oxide nanoparticles, detergent and demulsifier useful in the embodiments presently disclosed can vary depending on the desired application, the nature of the diesel fuel, and other desired components in the additive package or the finished fuel.

[0031] In another embodiment is provided a diesel fuel composition that comprises a major amount of a diesel fuel and a minor combustion improving amount of an additive composition comprising: a) one or more fuel-soluble component comprising one or more manganese and/or cerium compounds, mixtures or alloys; b) one or more fuel-soluble alkali or alkaline earth metal-containing detergents—e.g., one or more neutral or basic alkali or alkaline earth metal salts of at least one sulphonic acid, and/or at least one carboxylic acid, and/or at least one salicylic acid, and/or at least one alkylphenol, and/or at least one sulphurised alkylphenol; and c) a demulsifier of reduced phosphorus content as defined hereinabove, wherein component a) is present in an amount sufficient to supply from 0.1 to 5 ppm manganese or cerium or both to the fuel and component b) is present in an amount sufficient to supply from 5 to 50 ppm alkali and/or alkaline earth metal to the fuel composition. This embodiment can also contain one or more alkyl nitrate cetane number-improving agents.

[0032] By improving the conductivity of the fuel, the fuel is better able to dissipate a static charge that might be generated by high volume transportation of the fuel, such as when the fuel is dispensed into a tanker truck or rail car. Because the fuel is better able to dissipate a static charge, the fuel is less likely to generate a spark, which may ignite volatile fumes that might be present in the area, either from the fuel itself or from previous fuels that may have been transported in the tanker.

[0033] Certain of the present embodiments are based on the discovery by Applicants that the combination of cerium oxide nanoparticles and a dispersant/detergent provide an unexpected and surprising synergistic antistatic benefit to a middle distillate fuel. The embodiments also provide conductivity benefits without adding sulfur-containing compounds like the Stadis® antistatic agents to an ultra-low sulfur fuel, and thus provide an environmental benefit as well.

[0034] The embodiments are particularly suited for middle distillate fuel compositions. Middle distillate fuel compositions include, but are not limited to, jet fuels, diesel fuels, and kerosene. In an embodiment, the fuel is a low-sulfur fuel having less than about 50 ppm sulfur. In an embodiment, the fuel is an ultra-low sulfur diesel fuel or ultra-low sulfur kerosene. Ultra-low sulfur fuels are generally considered to have no more than about 15 ppm of sulfur, more preferably no more than 10 ppm of sulfur. The term "diesel fuel" is generally considered to be a generic term encompassing diesel, biodiesel, biodiesel-derived fuel, synthetic diesel and mixtures thereof. Although biodiesel is not technically a distillate fuel, it is nevertheless included within the definition of "middle distillate fuel compositions" as that term is used throughout this application and in the claims.

[0035] The present disclosure encompasses jet fuels, although these are conventionally not regarded as "low-sulfur" or "ultra-low sulfur" fuels since their sulfur levels can be comparatively quite high. Nevertheless, jet fuels may also benefit from the conductivity improvement of the embodiments regardless of their sulfur content.

[0036] The terms "combustion system" and "apparatus" used in the disclosure connote any apparatus, machine or motor that utilize, in whole or in part, a combustible fuel to generate power. The terms include, for example, diesel-electric hybrid vehicle, a gasoline-electric hybrid vehicle, a two-stroke engine, any and all burners or combustion units, including for example, stationary burners, waste incinerators, diesel fuel burners, diesel fuel engines, automotive diesel engines, gasoline fuel burners, gasoline fuel engines, power plant generators, and the like. The hydrocarbonaceous fuel combustion systems that may benefit from the present disclosure include all combustion units, systems, devices, and/or engines that burn fuels. The term "combustion system" also encompasses internal and external combustion devices, machines, engines, turbine engines, jet engines, boilers, incinerators, evaporative burners, plasma burner systems, plasma arc, stationary burners, and the like which can combust or in which can be combusted a hydrocarbonaceous fuel.

[0037] Cerium oxide nanoparticles have been used in diesel fuel applications as a catalyst for converters in the elimination of toxic exhaust emission gases. Cerium oxide has also shown utility in reducing the particulate emission from diesel engines. Envirox™ Fuel Borne Catalyst from Oxonica, Ltd. (Oxfordshire, England), for example, is a diesel fuel combustion improver which reduces fuel consumption and also reduces harmful exhaust emissions. Cerium oxide particles have also shown benefit of reducing haze and foam formation in diesel fuels.

[0038] Although it is possible to use ordinary cerium oxide particles it has been found to be beneficial in certain of the present embodiments to use cerium oxide which has been doped with components that result in additional oxygen vacancies being formed. This generally means that the dopant will be di- or tri-valent in order to provide oxygen vacancies. Such dopant ions must be di- or tri-valent ions of an element which is a rare earth metal, a transition metal or a metal of Group IIA, IIIB, VB, or VIB of the Periodic Table in order to provide oxygen vacancies. They must also be of a size that allows incorporation of the ion within the surface region of the cerium oxide nanoparticles. Accordingly metals with a large ionic radius should not be used.

[0039] Typically the doped oxides will have the formula $Ce_{1-x}M_xO_2$ where M is a said metal or metalloid, in particular Rh, Cu, Ag, Au, Pd, Pt, Sb, Se, Fe, Ga, Mg, Mn, Cr, Be, B, Co, V, Zr, Ti and Ca as well as Pr, Sm and Gd and x has a value up to 0.3, typically 0.01 or 0.1 to 0.2, or of the formula $[(CeO_2)_{1-n}(REO_y)_n]_{1-k}M'_k$ where M' is a said metal or metalloid other than a rare earth, RE is a rare earth, y is 1 or 1.5 and each of n and k, which may be the same or different, has a value op to 0.5, preferably up to 0.3, typically 0.01 or 0.1 to 0.2. Further details can be found in our PCT/GB2002/005013 to which reference should be made.

[0040] In general the cerium oxide particles will have a size not exceeding 1 micron and in particular embodiments will not exceed 300 nm in size, for example 1 to 300 nm, such as from 1 to 150 nm, in particular 1 to 50 nm, especially 1 to 20 nm.

[0041] In certain embodiments, it is preferred that the cerium oxide particles are coated to prevent agglomeration. For this purpose the particles can be comminuted in an organic solvent in the presence of a coating agent which is an organic acid, anhydride or ester or a Lewis base. It has been found that, in this way which involves coating in situ, it is possible to significantly improve the coating of the oxide. Further, the resulting product can, in many instances, be used directly without any intermediate step. Thus in some coating procedures it is necessary to dry the coated particles before dispersing them in a hydrocarbon solvent. Thus the cerium oxide particles can be dispersible or soluble in the fuel or another hydrocarbon compatible with the fuel.

[0042] The particles which are subjected to the process should have as large a surface area as possible and preferably the particles have a surface area, before coating, of at least 10 m·sup·**2**/g and preferably a surface area of at least 50 or 75 m^2/g, for example 80-150 m^2/g, or 100-300 m^2/g.

[0043] The coating process involves comminuting the particles so as to prevent any agglomerates from forming. Techniques which can be used for this purpose include high-speed stirring or tumbling and the use of a colloid mill, ultrasonics or ball milling. Ball milling is preferred. Further details of such coatings can be found in PCT/GB02/02312.

[0044] Typically the concentration of cerium oxide in the additive will be from 0.1 to 10%, generally 0.5 to 5%, by weight. Furthermore, the cerium oxide nanoparticles generally having a size not exceeding one micron and in one embodiment not exceeding 300 nm, for example 1 to 300 nm, such as from 1 to 150 nm, in particular 1 to 50 nm, and especially 1 to 20 nm.

[0045] It has been found that the cerium oxide particles can be stabilized in the fuel or fuel additive package by the presence of a detergent/dispersant. As noted, a synergistic antistatic effect is seen when the cerium oxide particles and/or doped cerium oxide particles are combined with a dispersant/detergent. Particular detergents which can be used in the present invention include a basic nitrogen-containing detergent. Suitable ashless detergents/dispersants include amides, amines, polyetheramines, Mannich bases and succinimides which are preferred, although metal-containing detergents are also effective herein.

[0046] These dispersants are described in numerous patent specifications, mainly as additives for use in lubricant compositions, but their use in hydrocarbon fuels has also been described. Ashless dispersants leave little or no metal-containing residue on combustion. They generally contain only carbon, hydrogen, oxygen and in most cases nitrogen, but sometimes contain in addition other non-metallic elements such as phosphorus, sulfur or boron. A particularly useful ashless dispersant/detergent herein is derived from "high reactive" polyisobutylene (HR-PIB) substituted on a maleic anhydride reacted with a polyamine to achieve a level of about 5.4% nitrogen to achieve enhanced dispersancy. Such a material is available from Afton Chemical Corporation as HiTEC® 4007. The detergent/dispersant can be used in the fuel additive packages herein at levels of from about 5 to about 20% by weight.

[0047] In one embodiment, the detergent is a succinimide, which has an average of at least 3 nitrogen atoms per molecule. The succinimide is preferably aliphatic and may be saturated or unsaturated, especially ethylenically unsaturated, e.g. an alkyl or alkenyl succinimide. Typically the detergent is formed from an alkyl or alkenyl succinic acylating agent, generally having at least 35 carbon atoms in the alkyl or alkenyl group, and an alkylene polyamine mixture having an average of at least 3 nitrogen atoms per molecule. In another embodiment the polyamine has 4 to 6 nitrogen atoms per molecule. Preferably it can be formed from a polyisobutenyl succinic acylating agent derived from polyisobutene having a number average molecular weight of 500 to 10,000 and an ethylene polyamine which can include cyclic and acyclic parts, having an average composition from triethylene tetramine to pentaethylene hexamine. Thus the chain will typically have a molecular weight from 500 to 2500, especially 750 to 1500 with those having molecular weights around 900 and 1300 being particularly useful although a succinimide with an aliphatic chain with a molecular weight of about 2100 is also useful. Further details can be found in U.S. Pat. Nos. 5,932,525 and 6,048,373 and EP-A 432,941, 460309 and 1,237,373.

[0048] Examples of suitable metal-containing detergents useful herein include, but are not limited to, such substances as lithium phenates, sodium phenates, potassium phenates, calcium phenates, magnesium phenates, sulphurised lithium phenates, sulphurised sodium phenates, sulphurised potassium phenates, sulphurised calcium phenates, and sulphurised magnesium phenates wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility; the basic salts of any of the foregoing phenols or sulphurised phenols (often referred to as "overbased" phenates or "overbased sulphurised phenates"); lithium sulfonates, sodium sulfonates, potassium sulfonates, calcium sulfonates, and magnesium sulfonates wherein each sulphonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility; the basic salts of any of the foregoing sulfonates (often referred to as "overbased sulfonates"; lithium salicylates, sodium salicylates, potassium salicylates, calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic substituents to impart hydrocarbon solubility; the basic salts of any of the foregoing salicylates (often referred to as "overbased salicylates"); the lithium, sodium, potassium, calcium and magnesium salts of hydrolysed phosphosulphurised olefins having 10 to 2000 carbon atoms or of hydrolysed phosphosulphurised alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2000 carbon atoms; lithium, sodium, potassium, calcium and magnesium salts of aliphatic carboxylic acids and aliphatic-substituted cycloaliphatic carboxylic acids; the basic salts of the foregoing carboxylic acids (often referred to as "overbased carboxylates" and many other similar alkali and alkaline earth metal salts of oil-soluble organic acids.

[0049] Mixtures of salts of two or more different alkali and/or alkaline earth metals can be used. Likewise, salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more calcium phenates with one or more calcium sulfonates) can also be used. While rubidium, cesium and strontium salts are feasible, their expense renders them impractical for most uses.

[0050] According to one embodiment of the present disclosure, the cerium oxide nanoparticles are added to diesel fuel at an early stage by being incorporated into the diesel fuel additive package. It has been found that incorporating the particles in this way can lead to improved fuel efficiency in the diesel engine by preventing agglomeration and hence loss of surface area of the cerium particles. The present disclosure improves the previous performance of cerium oxide particles or nanoparticles in fuel by allowing the cerium oxide to more fully perform its roles. This is achieved by reducing the cerium removal from the fuel by sediment formation thereby keeping more of the cerium atoms available for combustion catalysis and emission reduction or other benefits.

[0051] Another benefit of the present disclosure is reduced filter blockage of fuel filters because of the reduction in or elimination of sediment, precipitation and/or haze caused by, for example, interactions between the cerium atoms or particles and fuel additive components and/or contaminants. Malfunctioning fuel filters can lead to difficulties in engine operation and finally to a complete shut down. One example is the reduced interaction between phosphorus and the cerium oxide particles or nanoparticles according to the present disclosure to reduce fuel filter blockage. A measure of this benefit is observable from IP 387 Filtration Test. Thus, there is provided herein a method to reduce filter blockage of fuel filters in a vehicle or other apparatus employing a diesel engine combusting a diesel fuel and having a fuel filter, said method comprising adding to the diesel fuel prior to the introduction of the fuel to a vehicle or other apparatus a diesel fuel additive package comprising cerium oxide nanoparticles, a detergent and a demulsifier.

[0052] Accordingly, the present disclosure provides a method of improving the efficiency of a fuel for an internal combustion engine which comprises adding to the fuel prior to the introduction of the fuel to a vehicle or other apparatus comprising an internal combustion engine a fuel soluble metallic material containing cerium oxide and/or a manganese source, and a detergent and a demulsifier as fuel additives. By introducing the cerium oxide in this way there is little or no need for any vehicle fuel management system necessary by other methods of introduction such as on-board dosing. Fuel efficiency will result from the incorporation of the cerium oxide particles in the fuel.

[0053] Accordingly, the present disclosure also provides a fuel additive composition, which comprises cerium oxide nanoparticles and/or a manganese source together with a detergent, preferably an aliphatic succinimide and a demulsifier having less than about 8 mg/kg of phosphorus. In another embodiment the fuel additive composition further comprises a demulsifier, as defined hereinabove, and a cetane improver agent.

[0054] Typically the concentration of cerium oxide particles or nanoparticles in the diesel fuel additive will be from 0.1 to 10%, generally 0.5 to 5%, by weight.

[0055] Typically the fuel additives which are incorporated at a refinery may include cetane number improvers, cold flow improvers, antioxidants, and metal deactivators. Accordingly the fuel additive compositions of the present disclosure can incorporate one or more of these. Thus, the present disclosure provides fuel additive compositions comprising cerium oxide nanoparticles and/or colloids, a detergent, a demulsifier, and optionally one of more of the components selected from the group consisting of cetane number improvers (also called ignition improvers)(such as alkyl nitrates), cold flow improvers (such as polyesters), and antioxidants (such as phenolics eg. 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine), and metal deactivators such as salicylic acid derivatives, e.g. N,N-disalicylidene-1,2-propane diamine.

[0056] Lubricity additive, anti-rust agents and antifoamants are also useful in the diesel fuel additive packages of the present disclosure.

[0057] In another embodiment of the present disclosure, the fuel additive composition can contain a mixture, blend, compound of or alloy of two or more metals, plus a detergent/dispersant and a demulsifier with up to about 30 mg/kg of phosphorus. Mixed metal catalyst systems are known but the use thereof with detergents and a demulsifier able to reduce or eliminate haze, instability or precipitates is needed and presently provided.

[0058] Thus, an improved fuel additive composition of the present disclosure can comprise a material containing two or more metal-containing combustion catalysts, a detergent/dispersant, and a demulsifier having up to about 30 mg/kg of phosphorus. In another embodiment, the demulsifier has up to about 24 mg/kg, or in a separate example about 8 mg/kg to about 24 mg/kg, or in yet another example from about 0.1 mg/kg to about 8 mg/kg of phosphorus. The detergent/dispersant and the demulsifier can be, for example, as described hereinabove. These metal-containing combustion catalysts can be cerium oxide particles or nanoparticles, manganese sources, such as methylcyclopentadienyl manganese tricarbonyl, and iron sources, such as solubilized iron oxide and ferrocene.

[0059] By "manganese" herein is meant any manganese or manganese-containing material, compound or precursor, such as but not limited to methyl cyclopentadienyl manganese tricarbonyl, available from Afton Chemical Corporation as MMT®, and manganese sulfonate, manganese phenate, manganese salicylate, cyclopentadienyl manganese tricarbonyl, alkyl cyclopentadienyl manganese tricarbonyl, organic manganese tricarbonyl derivatives, alkyl cyclopentadienyl manganese derivatives, bis-cyclopentadienyl manganese, bis-alkyl cyclopentandienyl manganese, neutral and overbased manganese salicylates, neutral and overbased manganese phenates, neutral and overbased manganese sulfonates, manganese carboxylates, manganese oxide and combinations and mixtures thereof.

[0060] Therefore, a cerium/manganese mixture or alloy can be used herein; a cerium/manganese/iron mixture or alloy can be used herein; a cerium/iron mixture or alloy can be used herein; or a manganese/iron mixture or alloy can be used herein.

[0061] There is provided herein a fuel additive which comprises cerium oxide and a manganese source, a detergent, and a demulsifier with phosphorus content of up to about 24 mg/kg. In a separate example, the phosphorus in the demulsifier is about 8 mg/kg to about 24 mg/kg, or in yet another example from about 0.1 mg/kg to about 8 mg/kg of phosphorus.

[0062] Furthermore, cerium oxide particles or nanoparticles can be combined with ferrocene (an iron source) in the preparation of a fuel additive composition further comprising a detergent/dispersant and a demulsifier. Thus, for example, a fuel additive composition is provided comprising cerium oxide (e.g. Envirox™ from Oxonica), ferrocene (widely available), a succinimide detergent/dispersant (HiTEC® 4007 from Afton Chemical Corporation and derived from 950 MW polyisobutylene with greater than 70% vinylidene groups plus maleic anhydride, reacted with a polyamine to achieve a final N content of about 6.0%), and a demulsifier

(Tolad 9357 from Baker Petrolite) which will have excellent combustion improver activity, no haze or precipitate, good smoke reduction, and enhanced fuel economy.

[0063] The compositions and methods of certain of the present embodiments are capable of providing a conductivity to a fuel of at least 25 pS/m at the time and temperature of delivery. This conductivity is sufficient to meet the proposed new ASTM standard for conductivity in diesel fuels (ASTM D975 and amendments and appendices thereto) measured according to any appropriate test procedure, including but not limited to ASTM D2622 and ASTM D4951. The conductivity is obtained by the addition of the cerium oxide particles and the detergent alone, thus obviating the need to add conventional antistatic agents such as the Stadis® compounds. The conductivity benefit provided by the embodiments has been shown to be sustained for at least 7 days after the detergent and cerium oxide particles are combined together. An additional benefit of the present embodiments is that an antistatic effect is obtained without adding unnecessary sulfur to the fuel composition. For example, the combination of cerium oxide particles and detergent/dispersant can contribute no more than about 0.135 ppm of sulfur to the fuel composition, thus preserving the benefits of using ultra-low sulfur fuels.

EXAMPLES

[0064] Model Mixed Metal Systems

[0065] The following examples further illustrate aspects of the present disclosure but do not limit the present disclosure.

Example 1

[0066]

Cerium oxide (e.g. Envirox ™ from Oxonica)	1-200	ppm
Ferrocene (widely available)	5-30	weight %
Detergent/dispersant (HiTEC ® 4007 Afton Chemical)	5-15	weight %
Demulsifier (Tolad ® 9357 from Baker Petrolite)	1-10	weight %
Aromatic and/or aliphatic solvent(s)	45-89	weight %

[0067] HiTEC® 4656 Diesel Fuel Additive (Afton Chemical Corporation) is based on about 50% by weight of 2-ethyl hexyl nitrate cetane improver and 15% by weight of a HR-PIB succinimide detergent/dispersant with about 6.0 weight % nitrogen (HiTEC® 4007 available from Afton Chemical Corporation). HiTEC® 4656 was combined with 250 ppm of a source of cerium oxide particles in aliphatic solvent to deliver 5 ppm of cerium oxide particles (Envirox™ available from Oxonica). This combination can be used directly in a diesel fuel or diluted in aliphatic or aromatic solvent to prepare a diesel fuel additive.

Example 2

[0068]

Cerium/manganese alloy	1-200	ppm
Ferrocene (widely available)	5-30	weight %
Detergent/dispersant (HiTEC ® 4007 Afton Chemical)	5-15	weight %
Demulsifier (Tolad ® 9357 from Baker Petrolite)	1-10	weight %
Aromatic and/or aliphatic solvent(s)	45-89	weight %

[0069] To improve the fuel stability of the product of Example 1, it was combined with 2.27% weight percent demulsifier (Tolad® **9338**, a blend of long chain polyglycols, oxyalkylated phenol-formaldehyde resins and oxyalkylated adducts of glycol/epoxide polymers in aliphatic alcohols and an aromatic hydrocarbon solvent, available from Baker Petrolite). Tolad® 9338 had a phosphorus content of 23.95 mg/kg. However, there was a high degree of haze, which would be an unacceptable product for virtually all applications, depending on the shelf life needed and/or the type of diesel fuel involved. When filtered, sediment of 1.39 grams per 1 kg was obtained.

Example 3

[0070]

Cerium/manganese/iron alloy	1-200	ppm
Detergent/dispersant (HiTEC ® 4007 Afton Chemical)	5-15	weight %
Demulsifier (Tolad ® 9357 from Baker Petrolite)	1-10	weight %
Aromatic and/or aliphatic solvent(s)	45-89	weight %

[0071] To improve the solubility and fuel stability the product of Example 1 was combined with 2.27% by weight percent of a demulsifier (Tolad® 2898, an oxylated alkylphenolic resin with lower phosphorus content of 7.85 mg/kg). The fuel stability was improved and the haze reduced (see below) relative to the results for Example 2, but were not idealized for all fuels or all fuel applications. When filtered, sediment of 0.35 grams per 1 kg of additive product was obtained.

Example 4

[0072] The product of Example 1 was combined with 2.27% by weight percent of another demulsifier (Tolad® 9357, formaldehyde polymer with 4-(1,1-dimethylethyl)phenol, methyloxirane and oxirane in an aromatic solvent) which had a phosphorus content of 0.199 mg/kg. This fuel additive package had excellent clarity, very low haze, and no appreciable precipitate (only 0.15 grams of sediment per 1 kg of fuel additive package). This resulting diesel fuel additive package was combined with diesel fuel at a treat rate of 1350 ppm resulting in excellent fuel stability, no precipitate and no haze. In this final diesel fuel product the cerium oxide content was 0.37 weight % (5 ppm), and the phosphorus level is therefore only a trace amount. The final diesel fuel product was considered excellent in terms of smoke reduction, fuel economy, fuel stability, solubility and improved combustion.

[0073] As can be seen from the above examples, when HiTEC® 4656 Diesel Fuel Additive (alkyl nitrate cetane number improver) with Tolad® 9338 demulsifier was mixed with Enivrox™ cerium oxide nanoparticles the resulting fuel additive product produced a sediment of 1.39 grams per 1 kg of additive. When HiTEC® 4656 Diesel Fuel Additive (alkyl nitrate cetane number improver) with Tolad® 2898 demulsifier was mixed with Enivrox™ cerium oxide nanoparticles the product produced a sediment of 0.35 grams per 1 kg of additive. When HiTEC® 4656 Diesel Fuel Additive (alkyl nitrate cetane number improver) with Tolad 9357 demulsifier was mixed with Enivrox™ the product produced a sediment of 0.15 grams per 1 kg of additive.

[0074] Haze Measurements

Additive	Demulse	Envirox	Haze (NTU)
n/a	n/a	Y	335
H4656	T9338	N	5.74
H4656	T2898	N	5.61
H4656	T9357	N	5.18
H4656	T9338	Y	1552
H4656	T2898	Y	880
H4656	T9357	Y	175

[0075] Clearly the unexpected improvement is the reduction in haze when combining the cetane number improver, the cerium oxide nanoparticles, and a low phosphorus-containing demulsifier. "NTU" is a unit of measure known in the industry as "non-arbitrary units."

[0076] Defoaming Experiments

[0077] In addition, applicants carried out antifoam testing on the fuel additive products produced containing the alkyl nitrate cetane number improver and the cerium oxide nanoparticles with surprising results. It was observed that the cerium oxide has a positive influence on foam reduction. With the Envirox™ product alone, the fuel foam decay time was halved, but when used in conjunction with a HiTEC® 4656 type product, the foam performance was improved beyond the normal HiTEC® 4656 foam performance. Thus, an unexpected benefit is obtained in diesel fuel foam reduction when combining cerium oxide nanoparticles and an alkylnitrate cetane number improver.

				Day 0	
Fuel	Additive	Treat Rate (ppm)	Envirox (ppm)	Decay Time (sacs)	Foam Height (mols)
RF93-T-95	n/a	n/a	n/a	45	100
RF93-T-95	n/a	n/a	250	21.2	100
RF93-T-95	H4656	1100	n/a	6.9	80
RF93-T-95	H4656	1100	250	2.8	55

[0078] Base reference diesel fuel has a decay time of 45 seconds, with a foam height of 100 mls. Diesel fuel treated with 250 ppm Envirox™ has a decay time of 21.2 seconds and a foam height of 100 mls; diesel fuel treated with 1100 ppm HiTEC® 4656 has a decay time of 6.9 seconds and a foam height of 80 mls; and diesel treated with 250 ppm Envirox™ plus 1100 ppm HiTEC® 4656 has a decay time of 2.8 seconds and a foam height of 55 mls. Clearly, there is an unexpected excellent improvement in foam reduction achieved by combining the cerium oxide nanoparticles and the alkyl nitrate cetane number improver in the diesel fuel. Thus, there is provided herein a method for foam reduction in a diesel fuel by providing to the fuel a fuel additive package comprising cerium oxide nanoparticles and an alkyl nitrate cetane number improver additive.

[0079] By the incorporation of the present disclosure into vehicles or devices, significant improvements in mechanical design and methods of use are provided. In one embodiment herein is provided an emissions control system for the after-treatment of a diesel fuel combustion process exhaust stream comprising: an exhaust passageway for the passage of an exhaust stream containing exhaust byproducts from the combustion of a diesel fuel, a particulate filter selected from the group consisting of continuously regenerating technology diesel particulate filter, a diesel particulate filter, and a catalyzed diesel particulate filter, located within the exhaust passageway and adapted to contact the exhaust stream, wherein the fuel has an additive package introduced into it, the additive package comprising cerium oxide and/or manganese, a detergent, an alkyl nitrate ignition improver, and optionally a demulsifier, whereby the operation of the particulate filter is enhanced by maximizing the dispersancy of the cerium oxide. This prevents the agglomeration of the cerium oxide particles which would otherwise reduce the interaction of cerium oxide with the exhaust particulates. Furthermore, improved dispersing of the cerium oxide particles according to the present disclosure reduces their agglomeration and minimizes or eliminates the potential for fuel filter plugging. In addition, a method of use is provided for improving the performance of a diesel particulate filter by reducing the negative impact on the surface of the filter present in the absence of the use of the fuel additive packages described herein.

[0080] In certain engine designs, the injector nozzle holes are non-cylindrical but are flared outwardly with increasing diameter toward the combustion chamber with the intent to keep the injector hole dry after each injection of fuel. These designs are found to be extremely prone to coking which negatively impacts fuel flow, uniformity of combustion, and promotes deposit build-up because the fuel dynamic flow cannot sweep the surfaces of the injector holes clean. Therefore a need exists to protect the injector nozzle hole by improved exposure to the combustion chamber gases which will now include the cerium atoms and cerium oxide particles. By the present disclosure, the cerium and cerium oxide particles can serve to oxidize and remove the carbonaceous deposits in and around the nozzle hole. Thus is provided herein a method for use in a diesel engine having non-cylindrical injector nozzle holes of a diesel fuel additive package comprising cerium oxide, a detergent/dispersant, and a demulsifier having less than 24 mg/kg pf phosphorus. In a separate example, the phosphorus in the demulsifier is about 8 mg/kg to about 24 mg/kg, or in yet another example from about 0.1 mg/kg to about 8 mg/kg of phosphorus.

Conductivity Examples

[0081] Control 1

[0082] A sample of RF93-T-95 diesel fuel, which is a reference fuel containing 50-500 ppm of sulfur, was measured for conductivity according to IP 274 (ASTM D2624). The fuel was then subjected to an aging test in either a cold environment (@21° C.) or a hot environment (@50° C.). Two cold samples were used. After 7 days, the conductivity was again measured. The conductivity of the hot sample was measured directly out of the oven. One cold sample was allowed to sit at room temperature for 1 hour prior to measuring the conductivity, while the other cold sample was merely shaken after removing it from the refrigeration unit.

[0083] Control 2

[0084] Control 1 was repeated, except that 250 ppm (volume) of cerium oxide nanoparticles (Envirox™, average particle size=12 nm) were also added to the diesel fuel.

[0085] Example C1

[0086] Control 1 was repeated, except that 1100 ppm (volume) of a fuel additive concentrate HiTEC® 4656 (Afton Chemical) was added to the diesel fuel.

[0087] Example C2

[0088] The procedure for Example 1 was repeated, except that 250 ppm (volume) of cerium oxide nanoparticles (Envirox™, average particle size=12 nm) was also added to the diesel fuel before the additive concentrate was added.

[0089] Example C3

[0090] The procedure for Example 1 was repeated except that, instead of the fuel additive concentrate, 5 ppm (volume) of a traditional antistatic agent (Tolad® 3514 from Baker Petrolite) was added to the diesel fuel.

[0091] Example C4

[0092] The procedure for Example 3 was repeated except that 250 ppm (volume) of cerium oxide particles (as in Example 2) was also added to the diesel fuel.

[0093] Example C5

[0094] The procedure for Example 3 was repeated except that, instead of T3514, 5 ppm (volume) of another traditional antistatic agent (Stadis® 450 from Innospec Fuel Specialties) was added to the diesel fuel.

[0095] Example C6

[0096] The procedure for Example 5 was repeated except that 250 ppm (volume) of cerium oxide particles (as in Examples 2 and 4) was also added to the diesel fuel.

[0097] Controls 3-4

[0098] Controls 1-2 were repeated, except that an ultra-low sulfur diesel fuel containing 30 ppm of sulfur was used in place of the RF93-T-95 diesel fuel.

[0099] Examples C7-C12

[0100] Examples 1-6 were repeated using the ultra-low sulfur diesel fuel from Controls 3-4.

[0101] Results from the conductivity examples are reported in Table 1.

TABLE 1

Example	Antistatic Agent	Treat Rate (ppmv)	Cerium oxide	Day 0 Conductivity (pS)	Day 7 Conductivity (pS)	Day 7 Conductivity (pS)	Day 7 Conductivity (pS)
Control 1			N	153	214	160	154
Control 2			Y	188	290	201	192
C1			N	796	721	690	725
C2			Y	1197	690	550	523
C3	Tolad ® 3514	5	N	788	1438	1059	980
C4	Tolad ® 3514	5	Y	789	1232	992	816
C5	Stadis ® 450	5	N	421	772	541	479
C6	Stadis ® 450	5	Y	413	791	520	466
Control 3			N	109	176	128	131
Control 4			Y	132	174	135	151
C7			N	552	1070	735	700
C8			Y	884	1084	741	694
C9	Tolad ® 3514	5	N	245	323	281	256
C10	Tolad ® 3514	5	Y	281	340	282	268
C11	Stadis ® 450	5	N	405	560	431	379
C12	Stadis ® 450	5	Y	434	610	461	380

[0102] The data demonstrate a synergistic effect that the cerium oxide and detergent combination have on conductivity in diesel fuels. Moreover, the cerium oxide particles and detergent combination show higher initial conductivity and comparable or better aged conductivity as compared to traditional antistatic agents. Thus, the embodiments provide a conductivity benefit to a diesel fuel without the need to add special antistatic agents.

[0103] Other embodiments of the present disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the disclosure disclosed herein. As used throughout the specification and claims, "a" and/or "an" may refer to one or more than one. Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, percent, ratio, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the disclosure being indicated by the following claims.

We claim:

1. An additive concentrate for a middle distillate fuel composition, said additive concentrate comprising an antistatic agent, said antistatic agent comprising, in combination, a dispersant and cerium oxide particles.

2. The additive concentrate of claim **1**, wherein said fuel comprises a diesel fuel.

3. The additive concentrate of claim **1**, wherein said antistatic agent contributes no more than 0.135 ppm of sulfur to the additive concentrate.

4. The additive concentrate of claim **1**, wherein the cerium oxide particles comprise nanoparticles.

5. The additive concentrate of claim **1**, wherein said dispersant comprises a succinimide dispersant.

6. The additive concentrate of claim **7**, wherein said succinimide dispersant is formed from tetraethylene pentamine.

7. Use of the additive concentrate of claim **1** to provide a conductivity measure of at least 500 pS/m in a middle distillate fuel after aging for 7 days at 21° C.

8. A middle distillate fuel composition having improved conductivity, said fuel comprising an antistatic agent, said antistatic agent comprising, in combination, a dispersant and cerium oxide particles.

9. The fuel of claim **8**, wherein said fuel comprises a diesel fuel.

10. The fuel of claim **8**, wherein said antistatic agent contributes no more than 0.135 ppm of sulfur to the fuel composition.

11. The fuel of claim **8**, wherein said fuel has a conductivity of at least 500 pS/m after 7 days of aging at 21° C.

12. The fuel of claim **8**, wherein the cerium oxide particles comprise nanoparticles.

13. The fuel of claim **8**, wherein said dispersant comprises a succinimide dispersant.

14. The fuel of claim **13**, wherein said succinimide dispersant is formed from tetraethylene pentamine.

15. Use of the fuel of claim **8** in a combustion apparatus.

16. A method of dispensing a middle distillate fuel composition comprising the steps of adding to a middle distillate fuel composition an antistatic agent comprising, in combination, a dispersant and cerium oxide particles in an amount sufficient to provide a conductivity benefit to said fuel.

17. The method of claim **16**, further comprising the step of dispensing said fuel composition prior to the conductivity of said fuel composition dropping below 50 pS/m.

18. The method of claim **17**, wherein said dispensing step comprises dispensing said fuel composition into a bulk container.

19. The method of claim **16**, wherein said dispersant and said cerium oxide particles are pre-blended in an additive concentrate prior to addition to said fuel.

20. The method of claim **16**, wherein said fuel comprises a diesel fuel.

21. The method of claim **16**, wherein said antistatic agent contributes no more than 0.135 ppm of sulfur to the fuel composition.

22. The method of claim **16**, wherein said cerium oxide particles comprise nanoparticles.

23. The method of claim **16**, wherein said detergent comprises a succinimide detergent.

24. The method of claim **23**, wherein said succinimide dispersant is formed from tetraethylene pentamine.

25. A method of reducing a risk of ignition or explosion from static discharge, comprising the steps of providing a middle distillate fuel composition; adding a combination of a dispersant and cerium oxide particles to said fuel composition to improve conductivity in said fuel composition; thereby reducing the risk of static discharge in said fuel composition.

26. The method of claim **25**, further comprising the step of dispensing the fuel composition.

27. The method of claim **26**, wherein said dispensing step comprises dispensing said fuel composition into a bulk container.

28. The method of claim **26**, wherein the conductivity in said fuel composition is at least 50 pS/m at the time and temperature of delivery.

29. The method of claim **25**, wherein dispersant and said cerium oxide particles are pre-blended in an additive concentrate prior to being added to said fuel composition.

30. The method of claim **25**, wherein said fuel composition comprises a diesel fuel.

31. The method of claim **25**, wherein said middle distillate fuel is substantially free of a sulfur-containing conductivity improver.

32. The method of claim **25**, wherein the combination of dispersant and cerium oxide particles add no more than 0.135 ppm of sulfur to the fuel composition.

33. The method of claim **25**, wherein the cerium oxide particles comprise nanoparticles.

34. The method of claim **25**, wherein said dispersant comprises a succinimide dispersant.

35. The method of claim **34**, wherein said succinimide dispersant is formed from tetraethylene pentamine.

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