

## CERIUM OXIDE NANOPARTICLES AS FUEL ADDITIVES

5 This invention relates to cerium oxide nanoparticles which are useful as fuel additives.

Cerium oxide is widely used as a catalyst in three way converters for the elimination of toxic exhaust emission gases and the reduction in particulate emissions in automobiles. The ceria contained within the catalyst can act as a  
10 chemically active component, working as an oxygen store by release of oxygen in the presence of reductive gases, and removal of oxygen by interaction with oxidising species.

Cerium oxide may store and release oxygen by the following processes:-



The key to the use of ceria for catalytic purposes is the low redox potential between the  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  ions (1.7V) that allows the above reaction to easily occur in exhaust gases. Cerium oxide may provide oxygen for the oxidation of CO or  $\text{C}_n\text{H}_n$   
20 or may absorb oxygen for the reduction of  $\text{NO}_x$ . The amounts of oxygen reversibly provided in and removed from the gas phase are called the oxygen storage capacity (OSC) of ceria.

The above catalytic activity may occur when cerium oxide is added as an additive to fuel, for example diesel or petrol. However, in order for this effect to be  
25 useful the cerium oxide must be of a particle size small enough to remain in a stable dispersion in the fuel. The cerium oxide particles must be of a nanocrystalline nature, for example they should be less than 1 micron in size, and preferentially 1-300nm in size. In addition, as catalytic effects are surface area dependant the small particle size renders the nanocrystalline material more effective as a catalyst.

30 The incorporation of cerium oxide in fuel serves more than one purpose. The primary purpose is to act as a catalyst in the reduction of toxic exhaust gases on

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combustion of the fuel. However, it can serve another purpose in diesel engines. Diesel engines increasingly comprise a trap for particulates resulting from combustion of the diesel fuel. The presence of the cerium oxide in the traps helps to burn off the particulates which accumulate in the trap. Indeed such a use is in commercial operation. Thus certain vehicles, principally those devised by Peugeot, incorporate an on-board dosing system whereby cerium oxide is incorporated into the fuel before the latter enters the engine. This is, though, a complicated system and requires extensive electronic control to feed the appropriate amount of additive to the fuel. Effectively, the on-board system enables the particulate filter to be regenerated so that it lasts much longer.

The applicants have now found, according to the present invention, a different use for cerium oxide nanoparticles whereby the particles are added to fuel at an earlier stage. It has been found that incorporating the particles in this way can lead to improved fuel efficiency.

Accordingly, in a first aspect, there is provided 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 cerium oxide and/or doped cerium oxide and, optionally, one or more fuel additives.

By introducing the cerium oxide in this way there is no need for any vehicle fuel management system. Fuel efficiency will result from the incorporation of the cerium oxide particles in the fuel.

The particles can be incorporated into the fuel at various different points. There are particular advantages associated with their introduction at these various different points. In particular, the cerium oxide can be incorporated at the refinery, typically along with processing additives. This is, of course, the earliest point at which the cerium oxide can be added and it means that the fuel available at the refinery already contains the additive so that there is no need for it to be introduced at a later stage. However, if desired, it can be added at the fuel company's depot which means that the amount incorporated can be customised to the individual company's

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requirements. Alternatively, the cerium oxide can be added at the public or private filling station forecourt either to the storage tank or dispensed to the fuel on delivery to the vehicle; this has the advantage that there will be maximum stabilisation of the particle dispersion.

5 It will be appreciated that although the principal purpose of adding the cerium oxide to the fuel is to increase fuel economy, the presence of the particles in the fuel will, at the same time, help to regenerate a diesel particulate filter if present. The effect of the cerium oxide is generally to enable regeneration to take place at a lower temperature. This has the advantage that the filter which is usually of a ceramic  
10 material is generally less likely to crack.

Although it is possible to use ordinary cerium oxide particles it has been found to be beneficial 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.

15 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. For  
20 example transition metals in the first and second row of transition metals are generally preferred over those listed in the third. The ceria serves as the oxygen activation and exchange medium during a redox reaction. However, because ceria and the like are ceramic materials, they have low electronic conductivity and low activity surface sites for the chemisorption of the reacting species. Transition metal  
25 additives are particularly useful to improve this situation. In addition, multivalent dopants will also have a catalytic effect of their own.

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,  
30 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

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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 up 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 Application GB2002/005013 to which reference should be made.

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

It is preferred that the particles are coated to prevent agglomeration. For this purpose the particles can be comminuted in an organic solvent in the presence of a  
10 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  
15 in a hydrocarbon solvent.

Thus the cerium oxide can be dispersible or soluble in the (liquid) fuel or another hydrocarbon compatible with the fuel.

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  
20 coating, of at least 10 m<sup>2</sup>/g and preferably a surface area of at least 50 or 75 m<sup>2</sup>/g, for example 80-150 m<sup>2</sup>/g, or 100-300m<sup>2</sup>/g.

The coating agent is suitably an organic acid, anhydride or ester or a Lewis base. The coating agent is preferably an organic carboxylic acid or an anhydride, typically one possessing at least 8 carbon atoms, for example 10 to 25 carbon atoms,  
25 especially 12 to 18 carbon atoms such as stearic acid. It will be appreciated that the carbon chain can be saturated or unsaturated, for example ethylenically unsaturated as in oleic acid. Similar comments apply to the anhydrides which can be used. They are preferably dicarboxylic acid anhydrides, especially alkenyl succinic anhydrides, particularly dodecenylsuccinic anhydride, octadecenylsuccinic anhydride and  
30 polyisobutenyl succinic anhydride. Other organic acids, anhydrides and esters which

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can be used in the process of the present invention include those derived from phosphoric acid and sulphonic acid. The esters are typically aliphatic esters, for example alkyl esters where both the acid and ester parts have 4 to 18 carbon atoms.

The coating process can be carried out in an organic solvent. Preferably, the solvent is non-polar and is also preferably non-hydrophilic. It can be an aliphatic or an aromatic solvent. Typical examples include toluene, xylene, petrol, diesel fuel as well as heavier fuel oils. Naturally, the organic solvent used should be selected so that it is compatible with the intended end use of the coated particles. The presence of water should be avoided; the use of an anhydride as coating agent helps to eliminate any water present.

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.

It can be pointed out that the concentration of cerium oxide in the fuel can generally be less than that used in an on-board dosing system. Thus the concentration of cerium oxide in the fuel generally does not exceed 20 ppm and typically not exceed 10 ppm. In general, the minimum concentration is of the order of 1-2 ppm.

The particles can be incorporated into the fuel directly or as part of an additive package which is added to the fuel. The particles are preferably incorporated into diesel fuel. The present invention is particularly useful for large vehicles such as trucks and buses where an on-board dosing system would generally not be incorporated. The fuel can also be used for static engines such as generators.

The nature of the formulation used to incorporate the cerium oxide will, of course, vary depending on the point at which the cerium oxide is introduced.

In general it has been found that the cerium oxide particles can be stabilised in the fuel or fuel additive package by the presence of a detergent. In this connection it will be appreciated that lubricity agents can have an adverse effect since these can

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cause a precipitate to form. Particular detergents which can be used in the present invention include a basic nitrogen-containing detergent. Such detergents should be ashless i.e. they contain no metals. Suitable detergents include amides, amines, Mannich bases and succinimides which are preferred. Preferably 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. 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 US-A-5,932,525 and 6048373 and EP-A-432,941, 460309 and 1,237,373.

Accordingly, in a second aspect, there is provided a fuel additive composition which comprises cerium oxide and/or doped cerium oxide together with a detergent, preferably an aliphatic succinimide.

Typically the concentration of cerium oxide in the additive will be from 0.1 to 10%, generally 0.5 to 5%, by weight.

If cerium oxide is to be added at the refinery it may, in fact, be added without anything else. Typically the additives which are incorporated at the refinery include cetane number improvers, cold flow improvers and antioxidants. Accordingly the composition of the present invention can incorporate one or more of these. However since, in general, cerium oxide does not improve the cetane value it is unlikely that it would be added with these.

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If the cerium oxide is added at the depot then it can be added alone or with the detergent as well as the other ingredients which are typically added to the fuel at this stage as indicated below.

If the cerium oxide is added at the filling station forecourt then similar  
5 considerations apply to the depot addition.

Typical additives which can be used in the fuel compositions, especially diesel fuel, include those conventionally used, such as:-

**Non polar organic solvents** such as aromatic and aliphatic hydrocarbons such as toluene, xylene and white spirit, and mixtures thereof and those sold under  
10 the Trade Mark "SHELLSOL" by the Royal Dutch/Shell Group, and "EXXSOL" by ExxonMobil Group.

**Polar organic solvents**, in particular, alcohols generally aliphatic alcohols e.g. 2-ethylhexanol, decanol and isotridecanol,

**Detergents** such as hydrocarbyl-substituted amines and amides, e.g. hydro  
15 carbyl-substituted succinimides, e.g. a polyisobutenyl succinimide,

**Dehazers**, e.g. alkoxylated phenol formaldehyde polymers such as those commercially available as "NALCO" (Trade Mark) 7D07 (ex Nalco), and "TOLAD" (Trade Mark) 2683 (ex Petrolite),

**Anti-foaming agents** e.g. polyether-modified polysiloxanes, commercially  
20 available as "TEGOPREN" (Trade Mark) 5851 (ex Th. Goldschmidt) Q 25907 (ex Dow Corning) or "RHODORSIL" (Trade Mark) (ex Rhone Poulenc))

**Ignition improvers** such as aliphatic nitrates e.g. 2-ethylhexyl nitrate and cyclohexyl nitrate,

**Anti-rust agents** e.g. those sold commercially sold by Rhein  
25 Chemie, Mannheim, Germany as "RC 4801", or by Ethyl corporation as HiTEC (trade mark) 536, - or polyhydric alcohol esters of succinic acid derivatives

**Reodorants**,

**Anti-oxidants** e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine,

30 **Metal deactivators** such as salicylic acid derivatives, e.g. N, N<sup>1</sup>-

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disalicylidene-1,2-propane diamine and,

**Lubricity agents** such as polar compounds, especially fatty acids, esters and amides. Typically acids possess a  $C_2 - C_{50}$  chain and/or are aromatic and include poly basic acids such as dicarboxylic acids, for example a dimer of an unsaturated acid  
5 such as oleic or linoleic acid, as well as hydroxy aromatic carboxylic acids, especially with an ortho OH group, for example salicylic acid, especially those which are substituted by a group possessing at least 10 carbon atoms. Typical esters are derived from such acids and an alcohol which is typically a  $C_1$  and  $C_5$  aliphatic alcohol or a polyhydric alcohol such as a glycol, glycerol or pentaerythritol or poly(oxyalkylene)  
10 alcohol, e.g. with 5 oxyalkylene groups. The esters of a poly basic acid can be partial. Specific esters include glycerol mono- and di-esters such as glyceryl monooleate, sorbitan monooleate and pentaerythritol monooleate as well as salicylic esters. Other lubricity agents which may be used include esters derived from a carboxyphenol and a polyol and aminoalkylmorpholines. Some such agents are  
15 commercially available as EC831, P631, P633 or P639 (ex Infinium) or "HITEC" (Trade Mark) 580 (ex Ethyl Corporation), TOLAD 2670 and 9103 from Baker Petrolit and those described in WO 98/01516 and 98/16596.

Demulsifiers e.g. that commercially available as TOLAD 2898 from Baker Petrolite.

Preferred additives include one or more of an anti-foam, demulsifier and an  
20 anti-rust agent.

Unless otherwise stated, the (active matter) concentration of each additive in the fuel is generally up to 1000 ppmw (parts per million by weight of the diesel fuel), in particular up to 800 ppmw, e.g. 1 to 1000, 1 to 800 or 1-20, ppmw.

The (active matter) concentration of the dehazer in the diesel fuel is  
25 preferably in the range from 1 to 20ppmw. The (active matter) concentrations of other additives (with the exception of the detergent, ignition improver and the lubricity agent) are each preferably up to 20ppmw. The (active matter) concentration of the detergent is typically up to 800ppmw e.g. 10 to 500 ppmw. The (active matter) concentration of the ignition improver in the diesel fuel is preferably up to 600ppmw  
30 e.g. 100 to 250 ppmw. If a lubricity agent is incorporated into the diesel fuel, it is

conveniently used in an amount of 50 to 500 ppmw.

Some of these additives are more commonly added directly (with the cerium oxide) at the refinery while the others form part of a diesel fuel additive (DFA), typically added at the point of loading with the tanker or at the pump. A typical DFA

5 comprises:

|    |                   |                    |
|----|-------------------|--------------------|
|    | detergent         | 10-70% (by weight) |
|    | antirust          | 0-10%              |
|    | antifoam          | 0-10%              |
|    | dehazer           | 0-10%              |
| 10 | non-polar solvent | 0-50%              |
|    | polar solvent     | 0-40%              |

The diesel oil itself may be an additised (additive-containing) oil. If the diesel oil is an additised oil, it will contain minor amounts of one or more additives, e.g. anti-static agents, pipeline drag reducers, flow improvers, e.g. ethylene/vinyl acetate copolymers or acrylate/maleic anhydride copolymers, and wax anti-settling agents, e.g. those commercially available under the Trade Marks "PARAFLOW" (e.g. "PARAFLOW" 450; ex Paramins), "OCTEL" (e.g. "OCTEL" W 5000; ex Octel) and "DODIFLOW" (e.g. "DODIFLOW" V 3958; ex Hoechst).

The same or similar additives can be used for other fuels such as petrol, as one skilled in the art will appreciate.

The following Example further illustrates the present invention:

#### EXAMPLE

The settling of fuel containing cerium oxide alone or with other additives was tested with the following results:

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1. 2% Cerium Oxide in aliphatic solvent      48.0%  
     Shellsol D70      52.0% Aliphatic solvent  
     Significant solid separation after 24 hrs

- 30 2. 2% Cerium Oxide in aliphatic solvent      48.0%

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HITEC 4620

52.0% aliphatic solvent which contains  
detergent and antifoam

Slight solid separation after 24 hrs

5 3. 2% Cerium Oxide in aliphatic solvent 48.0%

BASF Keropur DP403

52.0% aliphatic solvent which contains  
detergent and antifoam

Slight solid separation after 24 hrs

10 4. 2% Cerium Oxide in aliphatic solvent 48.0%

Octel DFA

52.0% aliphatic solvent which contains  
detergent, antifoam and anticorrosion  
agent.

No solid separation after 24hrs.

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## CLAIMS

1. 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, cerium oxide and/or doped cerium oxide, a detergent and, optionally, one or more fuel additives.  
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2. A method according to claim 1 wherein the cerium oxide is doped with a divalent or trivalent metal or metalloid which is a rare earth metal, a transition metal or a metal of group IIA, IIIB, VB or VIB of the Periodic Table.  
10
3. A method according to claim 2, wherein the metal is rhodium, copper, silver, gold, palladium, platinum, iron, manganese, chromium, cobalt, vanadium, zirconium, titanium, terbium, praseodymium, samarium, gadolinium, antimony, selenium, gallium, magnesium, beryllium, boron or calcium.  
15
4. A method according to any one of the preceding claims wherein the cerium oxide and/or doped cerium oxide has a size not exceeding 1 micron.  
20
5. A method according to according to claim 4 wherein the cerium oxide and/or doped cerium oxide has a size from 1 to 300 nm.
6. A method according to any one of the preceding claims wherein the cerium oxide and/or doped cerium oxide is coated with an organic acid, anhydride or ester or a Lewis base.  
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7. A method according to claim 6, wherein the cerium oxide and/or doped cerium oxide is coated with a dicarboxylic acid anhydride.  
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8. A method accordingly to claim 7, wherein the cerium oxide and/or doped cerium oxide is coated with an alkenyl succinic anhydride.

9. A method accordingly to claim 8, wherein the succinic anhydride is dodecenyl succinic anhydride, octadecenyl succinic anhydride or polyisobutenyl succinic anhydride.
- 5 10. A method according to any one of the preceding claims, wherein the fuel is diesel fuel.
11. A method according to any one of the preceding claims, wherein the cerium oxide and/or doped cerium oxide is added with a solvent which is an aliphatic or aromatic hydrocarbon or an aliphatic alcohol.  
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12. A method according to any one of the preceding claims, wherein the cerium oxide and/or doped cerium oxide is added to the fuel at a refinery, or at a fuel depot, or at a filling station forecourt.  
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13. A method according to any one of the preceding claims, wherein the cerium oxide and/or doped cerium oxide is added together with one or more of a detergent, dehazer, anti-foaming agent, ignition improver, anti-rust agent, reodorant, anti-oxidant, metal deactivator, lubricity agent or a demulsifier.  
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14. A method according to claim 13, wherein the cerium oxide and/or doped cerium oxide is added together with a detergent.
15. A method according to claim 14 wherein the detergent is a basic nitrogen-containing ashless detergent.  
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16. A method according to claim 14 wherein the detergent is an amide, amine, Mannich base or succinimide.
- 30 17. A method according to claim 16 wherein the detergent is a hydrocarbyl-substituted amine or hydrocarbyl-substituted amide.
18. A method according to claim 16 wherein the detergent is a succinimide which has an average of at least 3 nitrogen atoms per molecule.

19. A method according to claim 18 wherein the succinimide is derived from an alkyl or alkenyl succinic acylating agent having at least 35 carbon atoms in the alkyl or alkenyl part and an alkylene polyamine mixture having an average of  
5 at least 3 nitrogen atoms per molecule.
20. A method according to claim 18 wherein the succinimide is derived from a polyisobutenyl succinic acylating agent obtainable from a polyisobutene having a number average molecular weight of 500 to 10,000 and an ethylene  
10 polyamine having an average composition from triethylene tetramine to pentaethylene hexamine.
21. A method according to claim 19 wherein the aliphatic chain of the succinimide has a molecular weight 500 to 2500.  
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22. A method according to claim 21 wherein the aliphatic chain of the succinimide has a molecular weight 750 to 1500.
23. A method according to any one of the preceding claims wherein the cerium  
20 oxide and/or doped cerium oxide particles are incorporated into the fuel directly, or as part of an additive package comprising said one or more fuel additives.
24. A method according to any one of the preceding claims, wherein a fuel  
25 additive composition comprises the cerium oxide and/or doped cerium oxide and the detergent, wherein the concentration of cerium oxide and/or doped cerium oxide in the additive is from 0.1 to 10% by weight.
25. A method according to claim 24, wherein the concentration of cerium oxide  
30 and/or doped cerium oxide in the additive is from 0.5 to 5% by weight.
26. A method according to any one of the preceding claims wherein the cerium oxide and/or doped cerium oxide is added at a concentration not exceeding 20 ppm.

27. A method according to claim 26 wherein the cerium oxide and/or doped cerium oxide is added in an amount not exceeding 10 ppm.
28. A fuel additive which comprises cerium oxide and/or doped cerium oxide and a detergent.
29. A fuel additive according to claim 28 wherein the detergent is as defined in any one of claims 15 to 22.
30. A fuel additive according to claim 28 or 29 wherein the concentration of cerium oxide and/or doped cerium oxide is from 0.1 to 10% by weight.
31. A fuel additive according to claim 30, wherein the concentration of cerium oxide and/or doped cerium oxide is from 0.5 to 5% by weight.
32. A fuel additive according to any one of claims 28 to 31, wherein the cerium oxide is as defined in one or more of claims 2 to 9.
33. A fuel additive according to claim 29 or 32 wherein at least one of additive selected from an anti-foaming agent, demulsifier and an anti-rust agent is added to the fuel.
34. A fuel additive according to any one of claims 28 to 33 which includes a solvent which is an aliphatic or aromatic hydrocarbon or an aliphatic alcohol.
35. A fuel additive according to claim 28 comprising cerium oxide and/or doped cerium oxide particles as part of an additive package comprising one or more fuel additives selected from a detergent, dehazer, anti-foaming agent, ignition improver, anti-rust agent, reodorant, anti-oxidant, metal deactivator, lubricity agent or demulsifier.