Claims

1. A method of reducing the emission of particulates having a diameter of less than 2.5 microns from a direct injection spark ignition engine, the method comprising combusting in the engine a gasoline composition comprising as an additive one or more quaternary ammonium compounds; wherein the level of particulates released via the exhaust stream of the direct injection spark ignition engine is lower than that achieved on combustion of the same fuel without the additive in the same engine.

2. The use of one or more quaternary ammonium compounds as an additive in a gasoline composition to reduce the emission of particulates having a diameter of less than 2.5 microns from a direct injection spark ignition engine; wherein the level of particulates via the exhaust stream of the direct injection spark ignition engine on combustion of a gasoline fuel comprising the additive is lower than that achieved on combustion of the same fuel without the additive in the same engine.

3. A method or use according to claim 1 or 2 wherein the or each quaternary ammonium compound is the reaction product of a nitrogen-containing species having at least one tertiary amine group and a quaternising agent wherein the nitrogen-containing species having at least one tertiary amine group may be selected from:

   (i) the reaction product of a hydrocarbyl-substituted acylating agent and a compound comprising at least one tertiary amine group and a primary amine, secondary amine or alcohol group;

   (ii) a Mannich reaction product comprising a tertiary amine group;

   (iii) a polyalkylene substituted amine having at least one tertiary amine group;

   (iv) a tertiary amine of formula $R^5R^6R^7N$, wherein each of R^5, R^6 and R^7 is independently an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group;

   (v) a cyclic tertiary amine; and

   (vi) a polyetheramine compound.

4. A method or use according to claim 3 wherein the nitrogen-containing species having at least one tertiary amine group is the reaction product of an alcohol or amine including a tertiary amino group and an optionally substituted succinic acid or anhydride thereof.

5. A method or use according to claim 4 wherein the succinic acid or anhydride thereof is substituted with a hydrocarbyl group and the hydrocarbyl substituted acylating agent includes an average of at least 1.2 succinic acid moieties per molecule.

6. A method or use according to claim 4 or claim 5 wherein the succinic acid or anhydride thereof is substituted with a polyisobutenyl group having a number average molecular weight of from 170 to 2800, preferably 450 to 1500.

7. A method or use according to any of claims 3 to 6 wherein the alcohol or amine including a tertiary amino group is selected from dimethylaminopropanol, dimethylaminopropylamine, N,N-diethyl-1,3- diaminopropane, N,N-dimethylethylenediamine, N,N-diethylethylenediamine, N,N-dibutylethylenediamine, or combinations thereof.

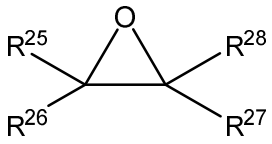
8. A method or use according to any of claims 3 to 7 wherein the quaternising agent is selected from esters of a carboxylic acid, dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl substituted epoxides optionally in combination with an acid, alkyl halides, alkyl sulfonates, sultones, hydrocarbyl substituted phosphates, hydrocarbyl substituted borates, alkyl nitrites, alkyl nitrates, hydroxides, N-oxides, chloroacetic acid or salts thereof, or mixtures thereof.

9. A method or use according to claim 8 wherein the quaternising agent is an ester of formula $R^{18}COOR^{19}$ wherein R^{19} is a C_1 to C_7 alkyl group and R^{18} is the residue of a carboxylic acid selected from a substituted aromatic carboxylic acid, an α-hydroxycarboxylic acid and a polycarboxylic acid.

10. A method or use according to claim 9 wherein the quaternising agent is an ester of a carboxylic acid selected from one or more of oxalic acid, phthalic acid, salicylic acid, maleic acid, malonic acid, citric acid, nitrobenzoic acid, aminobenzoic acid and 2, 4, 6-trihydroxybenzoic acid.

11. A method or use according to claim 10 wherein the quaternising agent is selected from dimethyl oxalate, methyl 2-nitrobenzoate, dimethylphthalate, dimethyltartrate and methyl salicylate

12. A method or use according to claim 8 wherein the quaternising agent is selected from epoxides, optionally in combination with an acid, wherein the epoxide has the formula:



wherein each of R^{25}, R^{26}, R^{27}, $R^{28/}$ is independently selected from hydrogen or an optionally substituted alkyl, alkenyl or aryl group, provided at least one of R^{25}, R^{26}, R^{27} and R^{28} is hydrogen.

13. A method or use according to claim 12 wherein each of R^{25}, R^{26} and R^{27} is hydrogen and R^{28} is selected from phenyl, an optionally substituted alkyl or alkenyl group having 1 to 20 carbon atoms, hydrogen, CH_2OR^{29} or CH_2OCOR^{30} wherein each of R^{29} and R^{30} is an optionally substituted alkyl or aryl group having from 1 to 20 carbon atoms.

14. A method or use according to claim 13 or claim 14 wherein the epoxide is selected from styrene oxide, ethylene oxide, propylene oxide, butylene oxide, stilbene oxide and isopropyl glycidyl ether.

15. A method or use according to any of claims 8, 12, 13 or 14 wherein the epoxide quaternising agents are used in combination with an acid.

16. A method or use according to claim 15 wherein the acid is selected from:
    - a small simple acid selected from formic acid, acetic acid, propionic acid and butyric acid;
    - a fatty acid compound; and
    - a hydrocarbyl substituted phthalic acid or succinic acid derivative.

17. A method or use according to any preceding claim wherein the gasoline composition further comprises one or more additional components selected from:
    a) carrier oils
    b) acylated nitrogen compounds which are the reaction product of a carboxylic acid-derived acylating agent and an amine
    c) hydrocarbyl-substituted amines wherein the hydrocarbyl substituent is substantially aliphatic and contains at least 8 carbon atoms
    d) Mannich base additives comprising nitrogen-containing condensates of a phenol, aldehyde and primary or secondary amine; and
    e) polyether amines.

18. A method or use according to any preceding claim wherein the quaternary ammonium compound is present in the gasoline composition in an amount of from 0.5 to 50 ppm.