leakage and environmental pollution, or cause severe damage to equipment that can be dangerous and extremely costly to equipment operators. Too high doses can also cause problems. As well as the unnecessary expense, some additives can cause deposits on combustion and thus should be included at the minimum concentration needed to achieve a desired effect.

It is therefore extremely useful to be able to determine whether the correct amount of an additive or an additive composition has been dosed into a particular formulated fuel.

One way in which it is possible to measure the concentration of an additive is to include in an additive composition a marker compound whose concentration can be determined, for example by spectroscopic means. It is known to add certain fluorescent compounds to additive compositions for such purposes. The use of Rhodamine compounds is described, for example, in US2009/0319195.

Fluorescent markers are generally known. However the selection of a suitable marker for inclusion in a fuel composition is not a simple undertaking as there are a number of considerations to take into account. It is generally undesirable to include coloured markers since the resulting fuels may be confused with fuels to which dyes are deliberately added to indicate their use for off-road purposes (e.g. red dyed diesel).

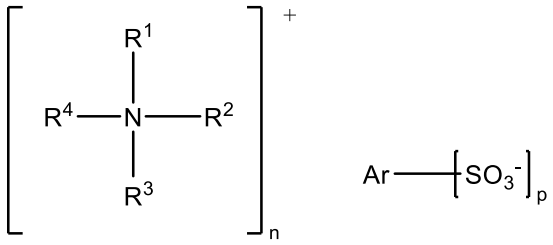
The use of markers including metallic species is also highly undesirable in fuels as their combustion may lead to increased deposits.

In addition, the solubility of any marker in a fuel or an additive concentrate composition comprising various components must be considered, as well as the potential interaction of the marker with other additives and/or other markers that may be present.

For the above reasons, and because fuels may comprise a number of additives, there is a continuing need to develop marker compounds for inclusion in fuel additive compositions.

Summary

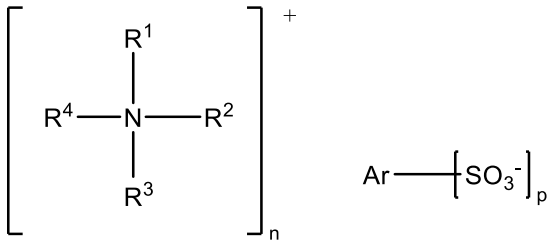
In one aspect, there is provided a compound of formula (I):



(I)

wherein p is 2 or 4, n is at least 1 and less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an unsubstituted alkyl, alkenyl or aralkyl group and each of R^2, R^3 and R^4 is independently an unsubstituted alkyl, alkenyl or aralkyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

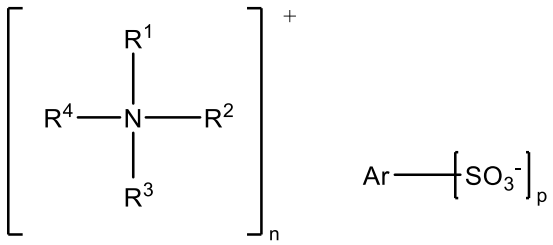
In another aspect, there is provided a method of preparing a compound of formula (I)



(I),

the method comprising admixing (a) a quaternary ammonium salt, a tertiary amine or a tertiary amine salt with (b) a sulfonated polycyclic aromatic compound; wherein p is 2 or 4, n is at least 1 and less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an unsubstituted alkyl, alkenyl or aralkyl group and each of R^2, R^3 and R^4 is independently an unsubstituted alkyl, alkenyl or aralkyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

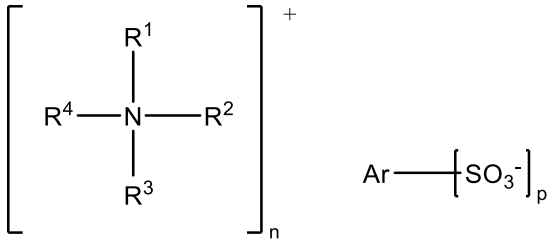
In yet another aspect, there is provided a composition comprising a compound of formula (I):



(I)

wherein p is 2 or 4, n is at least one and is less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an unsubstituted alkyl, alkenyl or aralkyl group and each of R^2, R^3 and R^4 is independently an unsubstituted alkyl, alkenyl or aralkyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

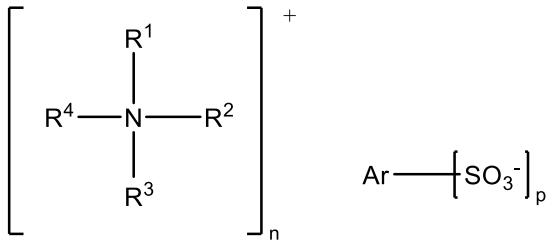
In a further aspect, there is provided a fuel composition comprising a fuel, one or more additives and a compound of formula (I):



(I)

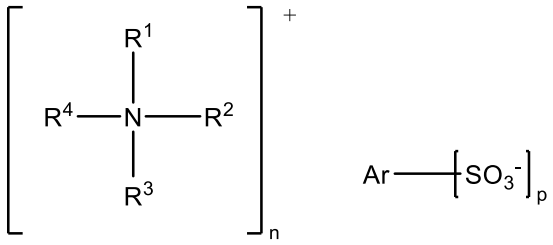
wherein p is at least 1, n is at least 1 and is less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an optionally substituted hydrocarbyl group and each of R^2, R^3 and R^4 is independently an optionally substituted hydrocarbyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

In another aspect, the present disclosure provides a method of preparing a fuel composition, the method comprising preparing an additive composition comprising as an additive a compound of formula (I)



wherein p is at least 1, n is at least 1 and is less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an optionally substituted hydrocarbyl group and each of R^2, R^3 and R^4 is independently an optionally substituted hydrocarbyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms; and dosing said additive composition into a fuel.

In yet another aspect, there is provided a use of a compound of formula (I) as a fluorescent marker:



(I)

wherein p is at least 1, n is at least 1 and is less than or equal to p; Ar is a polycyclic aromatic moiety, R^1 is hydrogen or an optionally substituted hydrocarbyl group and each of R^2, R^3 and R^4 is independently an optionally substituted hydrocarbyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

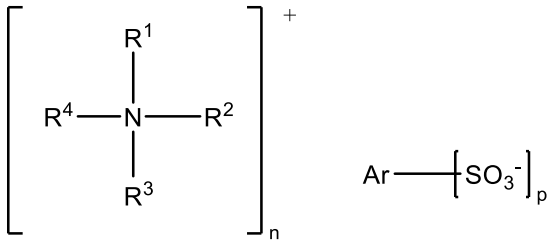
In a further aspect, there is provided a method of determining the presence of an additive in a fuel composition comprising said additive and a compound of formula (I) as described herein, the method comprising applying electromagnetic radiation having a first wavelength to said fuel composition; and determining the emission of electromagnetic radiation from the compound of formula (I) at a second wavelength.

In another aspect, there is provided a method of determining the concentration of a first additive in a fuel composition comprising said first additive and a compound of formula (I) as described herein, the compound of formula (I) being present in the fuel composition at a concentration that is proportional to the concentration of the first additive; the method comprising: applying electromagnetic radiation having a first wavelength to said fuel composition; measuring emission of electromagnetic radiation from the compound of formula (I) at a second wavelength; and calculating from the level of emission at said second wavelength the concentration of the first additive in the fuel composition.

In yet another aspect, there is provided a method of determining the concentration of an additive composition that has been dosed into a fuel composition, wherein the additive composition comprises a compound of formula (I) as described herein and at least one further additive; the method comprising: applying electromagnetic radiation having a first wavelength to said fuel composition; measuring emission of electromagnetic radiation from the compound of formula (I) at a second wavelength; and calculating from the level of emission at said second wavelength the concentration of the compound of formula (I) in the fuel composition.

In a further aspect, there is provided a kit for determining the concentration of a compound of formula (I) in a fuel composition, the kit comprising means for applying electromagnetic radiation having a first wavelength to said fuel composition; and means for measuring

emission of electromagnetic radiation at a second wavelength, wherein the compound of formula (I) has the structure:



(I)

wherein p is at least 1, n is at least 1 and is less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an optionally substituted hydrocarbyl group and each of R^2, R^3 and R^4 is independently an optionally substituted hydrocarbyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

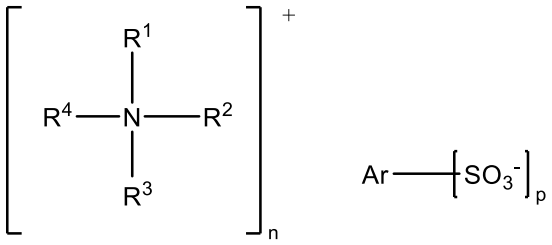
Detailed Description

The present inventors have prepared a class of novel marker compounds having advantageous properties that are suitable for use in fuel additive compositions.

According to a first aspect of the present invention there is provided a compound of formula (I):

Claims

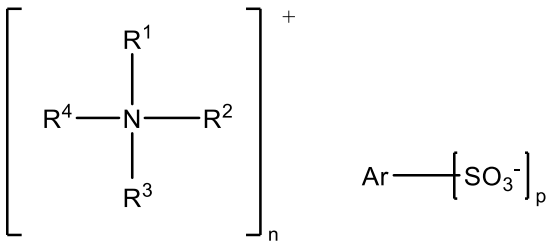
1. A compound of formula (I):



(I)

wherein p is 2 or 4, n is at least 1 and less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an unsubstituted alkyl, alkenyl or aralkyl group and each of R^2, R^3 and R^4 is independently an unsubstituted alkyl, alkenyl or aralkyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

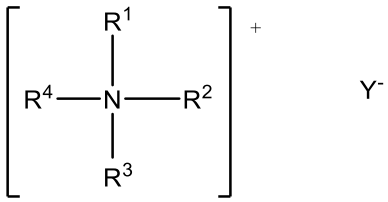
2. A method of preparing a compound of formula (I):



(I),

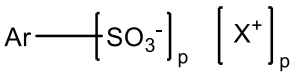
the method comprising admixing (a) a quaternary ammonium salt, a tertiary amine or a tertiary amine salt with (b) a sulfonated polycyclic aromatic compound; wherein p is 2 or 4, n is at least 1 and less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an unsubstituted alkyl, alkenyl or aralkyl group and each of R^2, R^3 and R^4 is independently an unsubstituted alkyl, alkenyl or aralkyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

3. A method of preparing a compound of formula (I) according to claim 2 in which component (a) comprises a quaternary ammonium salt or a tertiary amine salt, and the method involves admixing a compound of formula (III):



(III)

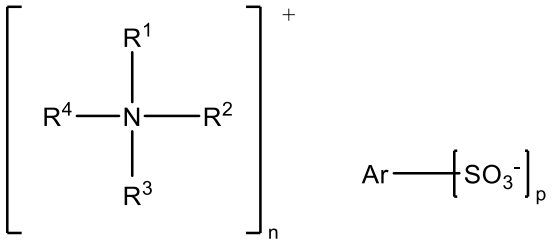
and compound of formula (IV):



(IV)

wherein Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, p is 2 or 4, X^+ is a proton, an ammonium ion or a metal ion, R^1 is hydrogen or an unsubstituted alkyl, alkenyl or aralkyl group, each of R^2, R^3 and R^4 is independently an unsubstituted alkyl, alkenyl or aralkyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms and Y^- is an anion.

4. A composition comprising a compound of formula (I):

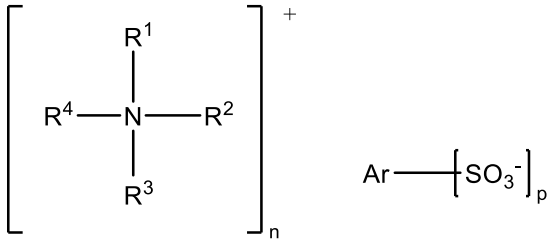


(I)

wherein p is 2 or 4, n is at least one and is less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an unsubstituted alkyl, alkenyl or aralkyl group and each of R^2, R^3 and R^4 is independently an unsubstituted alkyl, alkenyl or aralkyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

5. A composition according to claim 4 which is an additive composition for a fuel and which further comprises one or more fuel additives.

6. A fuel composition comprising a fuel, one or more additives and a compound of formula (I):



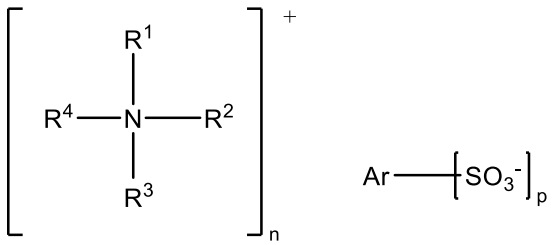
(I)

Wherein p is at least 1, n is at least 1 and is less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an optionally substituted hydrocarbyl group and each of R^2, R^3 and R^4 is independently an optionally substituted hydrocarbyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

7. A fuel composition according to claim 6 wherein the fuel comprises gasoline, ethanol or mixtures thereof.

8. A fuel composition according to claim 6 which comprises diesel.

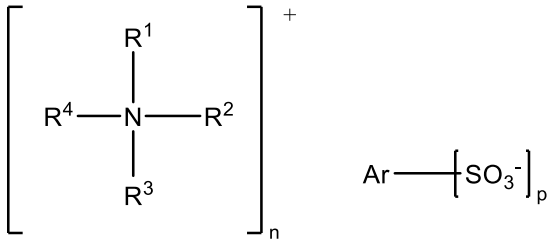
9. A method of preparing a fuel composition, the method comprising:
   - preparing an additive composition comprising as an additive a compound of formula (I)



   wherein p is at least 1, n is at least 1 and is less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an optionally substituted hydrocarbyl group and each of R^2, R^3 and R^4 is independently an optionally substituted hydrocarbyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms; and
   - dosing said additive composition into a fuel.

10. A method according to claim 9 which involves:
   - preparing said additive composition;
   - dosing said additive composition into an ethanol component of a fuel composition; and
   - blending said ethanol component with a gasoline fuel.

11. The use of a compound of formula (I):



(I)

as a fluorescent marker; wherein p is at least 1, n is at least 1 and is less than or equal to p; Ar is a polycyclic aromatic moiety, R^1 is hydrogen or an optionally substituted hydrocarbyl group and each of R^2, R^3 and R^4 is independently an optionally substituted hydrocarbyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

12. A method of determining the presence of an additive in a fuel composition comprising said additive and a compound of formula (I) as defined in claim 6, the method comprising applying electromagnetic radiation having a first wavelength to said fuel composition; and determining the emission of electromagnetic radiation from the compound of formula (I) at a second wavelength.

13. A method of determining the concentration of a first additive in a fuel composition comprising said first additive and a compound of formula (I) as defined in claim 6, the compound of formula (I) being present in the fuel composition at a concentration that is proportional to the concentration of the first additive; the method comprising: applying electromagnetic radiation having a first wavelength to said fuel composition; measuring emission of electromagnetic radiation from the compound of formula (I) at a second wavelength; and calculating from the level of emission at said second wavelength the concentration of the first additive in the fuel composition.

14. A method of determining the concentration of an additive composition that has been dosed into a fuel composition, wherein the additive composition comprises a compound of formula (I) as defined in claim 6 and at least one further additive; the method comprising: applying electromagnetic radiation having a first wavelength to said fuel composition; measuring emission of electromagnetic radiation from the compound of formula (I) at a second wavelength; and calculating from the level of emission at said

second wavelength the concentration of the compound of formula (I) in the fuel composition.

15. A composition, method or use according to any preceding claim wherein R^1 is hydrogen or an alkyl, alkenyl or alkaryl group having 1 to 12 carbon atoms and each of R^2, R^3 and R^4 is an alkyl, alkenyl or alkaryl group having 1 to 36 carbon atoms, provided that that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.

16. A composition, method or use according to any preceding claim wherein R^1 is hydrogen or an alkyl group having 1 to 4 carbon atoms, R^2 is benzyl or an alkyl group having 1 to 4 carbon atoms, and each of R^3 and R^4 is an alkyl, alkenyl or alkaryl group having 1 to 36 carbon atoms, provided that that at least one of R^3 and R^4 has at least 6 carbon atoms.

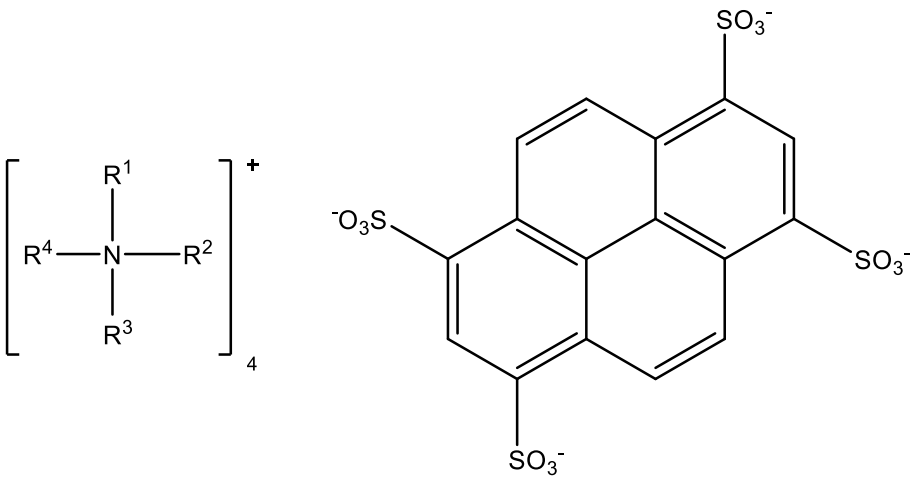
17. A composition, method or use according to any preceding claim wherein R^1, R^2, R^3 and R^4 together comprise in total from 16 to 40 carbon atoms, preferably from 20 to 36 carbon atoms, for example from 20 to 30 carbon atoms.

18. A composition, method or use according to any preceding claim wherein each of R^1, R^2, R^3 and R^4 is an unsubstituted alkyl or alkenyl group; and each of R^3 and R^4 has at least 6 carbon atoms.

19. A composition, method or use according to any preceding claim wherein R^1 is hydrogen or an unsubstituted alkyl group having 1 to 4 carbon atoms; R^2 is an unsubstituted alkyl group having 1 to 4 carbon atoms or an unsubstituted alkyl or alkenyl group having 6 to 36 carbon atoms, preferably 8 to 30 carbon atoms; R^3 is benzyl, an unsubstituted alkyl group having 1 to 4 carbon atoms or an unsubstituted alkyl or alkenyl group having 6 to 36 carbon atoms, preferably 8 to 30 carbon atoms; and R^4 is an unsubstituted alkyl or alkenyl group having 6 to 36 carbon atoms, preferably 8 to 30 carbon atoms.

20. A composition, method or use according to any preceding claim wherein n is from 1 to 4.

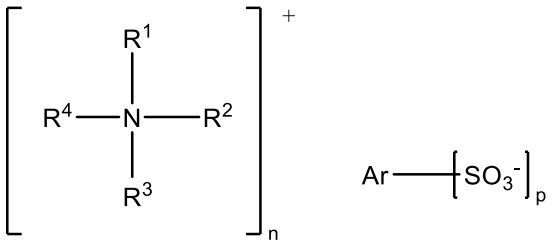
21. A composition, method or use according to any preceding claim wherein the compound of formula (I) has the structure (II):



(II)

or an isomer thereof.

22. A kit for determining the concentration of a compound of formula (I) in a fuel composition, the kit comprising means for applying electromagnetic radiation having a first wavelength to said fuel composition; and means for measuring emission of electromagnetic radiation at a second wavelength, wherein the compound of formula (I) has the structure:



(I)

wherein p is at least 1, n is at least 1 and is less than or equal to p; Ar is a polycyclic aromatic moiety based on a fluorene, anthracene or pyrene moiety or an isomer thereof, R^1 is hydrogen or an optionally substituted hydrocarbyl group and each of R^2, R^3 and R^4 is independently an optionally substituted hydrocarbyl group, provided that at least one of R^2, R^3 and R^4 has at least 6 carbon atoms.