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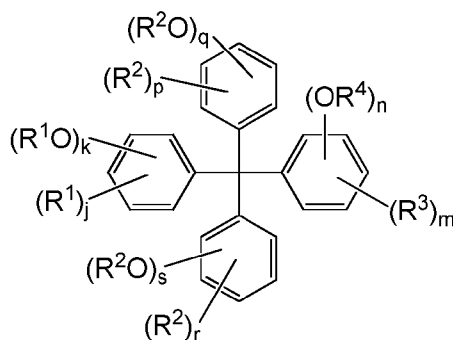
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(54) Title: ALKYL TRITYL PHENYL ETHERS



(I)

(57) Abstract: A compound having formula (I) wherein R<sup>1</sup> and R<sup>2</sup> independently represent C<sub>1</sub>-C<sub>6</sub> alkyl; R<sup>3</sup> is C<sub>1</sub>-C<sub>6</sub> alkyl; R<sup>4</sup> is C<sub>1</sub>-C<sub>18</sub> alkyl or C<sub>4</sub>-C<sub>18</sub> heteroalkyl; m is zero, one, two or three; n is one, two or three; and j, k, p, q, r and s independently are zero, one or two; provided that at least one of j, k, p, q, r and s is not zero.

**ALKYL TRITYL PHENYL ETHERS**

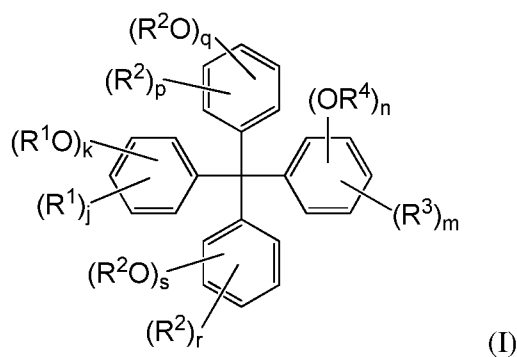
This invention relates to new compounds useful in a method for marking liquid hydrocarbons and other fuels and oils.

Marking of petroleum hydrocarbons and other fuels and oils with various kinds of chemical markers is well known in the art. A variety of compounds have been used for this purpose, as well as numerous techniques for detection of the markers, e.g., absorption spectroscopy and mass spectrometry. For example, U.S. Pat. No. 7,858,373 discloses the use of a variety of organic compounds for use in marking liquid hydrocarbons and other fuels and oils. However, there is always a need for additional marker compounds for these products. Combinations of markers can be used as digital marking systems, with the ratios of amounts forming a code for the marked product. Additional compounds useful as fuel and lubricant markers would be desirable to maximize the available codes. The problem addressed by this invention is to find additional markers useful for marking liquid hydrocarbons and other fuels and oils.

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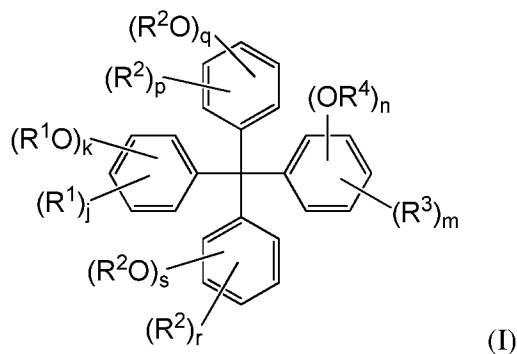
**STATEMENT OF INVENTION**

The present invention provides a compound having formula (I)



wherein  $R^1$  and  $R^2$  independently represent  $C_1$ - $C_6$  alkyl;  $R^3$  is  $C_1$ - $C_6$  alkyl;  $R^4$  is  $C_1$ - $C_{18}$  alkyl or  $C_4$ - $C_{18}$  heteroalkyl;  $m$  is zero, one, two or three;  $n$  is one, two or three; and  $j$ ,  $k$ ,  $p$ ,  $q$ ,  $r$  and  $s$  independently are zero, one or two; provided that at least one of  $j$ ,  $k$ ,  $p$ ,  $q$ ,  $r$  and  $s$  is not zero.

The present invention further provides a method for marking a petroleum hydrocarbon or a liquid biologically derived fuel; said method comprising adding to said petroleum hydrocarbon or liquid biologically derived fuel at least one compound having formula (I)



wherein  $R^1$  and  $R^2$  independently represent  $C_1$ - $C_6$  alkyl;  $R^3$  is  $C_1$ - $C_6$  alkyl;  $R^4$  is  $C_1$ - $C_{18}$  alkyl or  $C_4$ - $C_{18}$  heteroalkyl;  $m$  is zero, one, two or three;  $n$  is one, two or three; and  $j$ ,  $k$ ,  $p$ ,  $q$ ,  $r$  and  $s$  independently are zero, one or two; provided that at least one of  $j$ ,  $k$ ,  $p$ ,  $q$ ,  $r$  and  $s$  is not zero; and wherein each compound having formula (I) is present at a level from 0.01 ppm to 20 ppm.

#### DETAILED DESCRIPTION

Percentages are weight percentages (wt%) and temperatures are in  $^{\circ}\text{C}$ , unless specified otherwise. Concentrations are expressed either in parts per million (“ppm”) calculated on a weight/weight basis, or on a weight/volume basis (mg/L); preferably on a weight/volume basis. The term “petroleum hydrocarbon” refers to products having a predominantly hydrocarbon composition, although they may contain minor amounts of oxygen, nitrogen, sulfur or phosphorus; petroleum hydrocarbons include crude oils as well as products derived from petroleum refining processes; they include, for example, crude oil, lubricating oil, hydraulic fluid, brake fluid, gasoline, diesel fuel, kerosene, jet fuel and heating oil. Marker compounds of this invention can be added to a petroleum hydrocarbon or a liquid biologically derived fuel; examples of the latter are biodiesel fuel, ethanol, butanol, ethyl tert-butyl ether or mixtures thereof. A substance is considered a liquid if it is in the liquid state at  $20^{\circ}\text{C}$ . A biodiesel fuel is a biologically derived fuel containing a mixture of fatty acid alkyl esters, especially methyl esters. Biodiesel fuel typically is produced by transesterification of either virgin or recycled vegetable oils, although animal fats may also be used. An ethanol fuel is any fuel containing ethanol, in pure form, or mixed with petroleum hydrocarbons, e.g., “gasohol.” An “alkyl” group is a substituted or unsubstituted hydrocarbyl group having from one to twenty-two carbon atoms in a linear, branched or cyclic

arrangement. Substitution on alkyl groups of one or more OH or alkoxy groups is permitted; other groups may be permitted when specified elsewhere herein. Preferably, alkyl groups are saturated. Preferably, alkyl groups are unsubstituted. Preferably, alkyl groups are linear or branched. A "heteroalkyl" group is an alkyl group in which one or more methylene groups  
5 has been replaced by O or S. Preferably, heteroalkyl groups contain from one to six O or S atoms, preferably from one to four, preferably from one to three. The methylene groups replaced by O or S were bonded to two other carbon atoms in the corresponding alkyl group. Preferably, heteroalkyl groups do not contain S atoms. Heteroalkyl groups may be substituted by OH, SH or C<sub>1</sub>-C<sub>18</sub> alkoxy groups, preferably OH or C<sub>1</sub>-C<sub>6</sub> alkoxy groups,  
10 preferably hydroxy or C<sub>1</sub>-C<sub>4</sub> alkoxy groups. Examples of heteroalkyl groups include oligomers of ethylene oxide, propylene oxide or butylene oxide having two to six units of the alkylene oxide (preferably two to four, preferably two or three) and a terminal hydroxy or C<sub>1</sub>-C<sub>6</sub> alkoxy group (preferably hydroxy or C<sub>1</sub>-C<sub>4</sub> alkoxy, preferably hydroxy or methoxy, preferably hydroxy); an example of an ethylene oxide oligomer is  $-\{(\text{CH}_2)_2\text{O}\}_i\text{R}^2$ , where i is  
15 an integer from two to six and R<sup>2</sup> is hydrogen or C<sub>1</sub>-C<sub>6</sub> alkyl. Preferably, i is from two to four, preferably two or three. Preferably, R<sup>2</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably hydrogen or methyl, preferably hydrogen. Preferably, the compounds of this invention contain elements in their naturally occurring isotopic proportions.

Preferably, R<sup>1</sup> and R<sup>2</sup> independently are C<sub>1</sub>-C<sub>4</sub> alkyl; preferably methyl or ethyl;  
20 preferably methyl. Preferably, R<sup>1</sup> and R<sup>2</sup> are saturated. R<sup>1</sup>, OR<sup>1</sup>, R<sup>2</sup> and OR<sup>2</sup> may be at any available positions on the benzene rings to which they are attached, preferably the positions meta and para to the quaternary carbon to which all four benzene rings are attached. Preferably, j, k, p, q, r and s independently are zero or one. Preferably, k, q and s are zero. Preferably, q=s and p=r. Preferably, j is one. Preferably, p and r are one. Preferably, R<sup>4</sup> is  
25 C<sub>2</sub>-C<sub>12</sub> alkyl or C<sub>4</sub>-C<sub>12</sub> heteroalkyl, preferably C<sub>2</sub>-C<sub>12</sub> alkyl, preferably C<sub>3</sub>-C<sub>12</sub> alkyl, preferably C<sub>4</sub>-C<sub>12</sub> alkyl, preferably C<sub>4</sub>-C<sub>10</sub> alkyl, preferably C<sub>6</sub>-C<sub>10</sub> alkyl. Preferably, R<sup>4</sup> is saturated. Preferably, R<sup>4</sup> is linear or branched, preferably linear. Preferably, R<sup>3</sup> is C<sub>2</sub>-C<sub>6</sub> alkyl, preferably C<sub>3</sub>-C<sub>6</sub> alkyl, preferably C<sub>4</sub>-C<sub>6</sub> alkyl, preferably C<sub>3</sub>-C<sub>4</sub> alkyl, preferably sec-butyl, t-butyl or isopropyl. Preferably, R<sup>3</sup> is saturated. Preferably, R<sup>3</sup> is linear or branched,  
30 preferably branched. R<sup>3</sup> and OR<sup>4</sup> may be at any available position on the benzene ring to which they are attached, preferably the positions meta and para to the quaternary carbon to which all four benzene rings are attached. Preferably, when n is one, OR<sup>4</sup> is at the para position. Preferably m is zero, one or two; preferably zero or one. Preferably n is one or two, preferably one. Preferably, m is one and n is one. Preferably, n is two and m is zero. When

any of j, k, p, q, r, s, m and n is zero, the associated substituent is absent, e.g., when m is zero, R<sup>3</sup> is absent.

In using the compounds of this invention as markers, preferably the minimum amount of each compound added to a liquid to be marked is at least 0.01 ppm, preferably at least 0.02 ppm, preferably at least 0.05 ppm, preferably at least 0.1 ppm, preferably at least 0.2 ppm. Preferably, the maximum amount of each marker is 50 ppm, preferably 20 ppm, preferably 15 ppm, preferably 10 ppm, preferably 5 ppm, preferably 2 ppm, preferably 1 ppm, preferably 0.5 ppm. Preferably, the maximum total amount of marker compounds is 100 ppm, preferably 70 ppm, preferably 50 ppm, preferably 30 ppm, preferably 20 ppm, preferably 15 ppm, preferably 12 ppm, preferably 10 ppm, preferably 8 ppm, preferably 6 ppm, preferably 4 ppm, preferably 3 ppm, preferably 2 ppm, preferably 1 ppm. Preferably, a marker compound is not detectible by visual means in the marked petroleum hydrocarbon or liquid biologically derived fuel, i.e., it is not possible to determine by unaided visual observation of color or other characteristics that it contains a marker compound. Preferably, a marker compound is one that does not occur normally in the petroleum hydrocarbon or liquid biologically derived fuel to which it is added, either as a constituent of the petroleum hydrocarbon or liquid biologically derived fuel itself, or as an additive used therein.

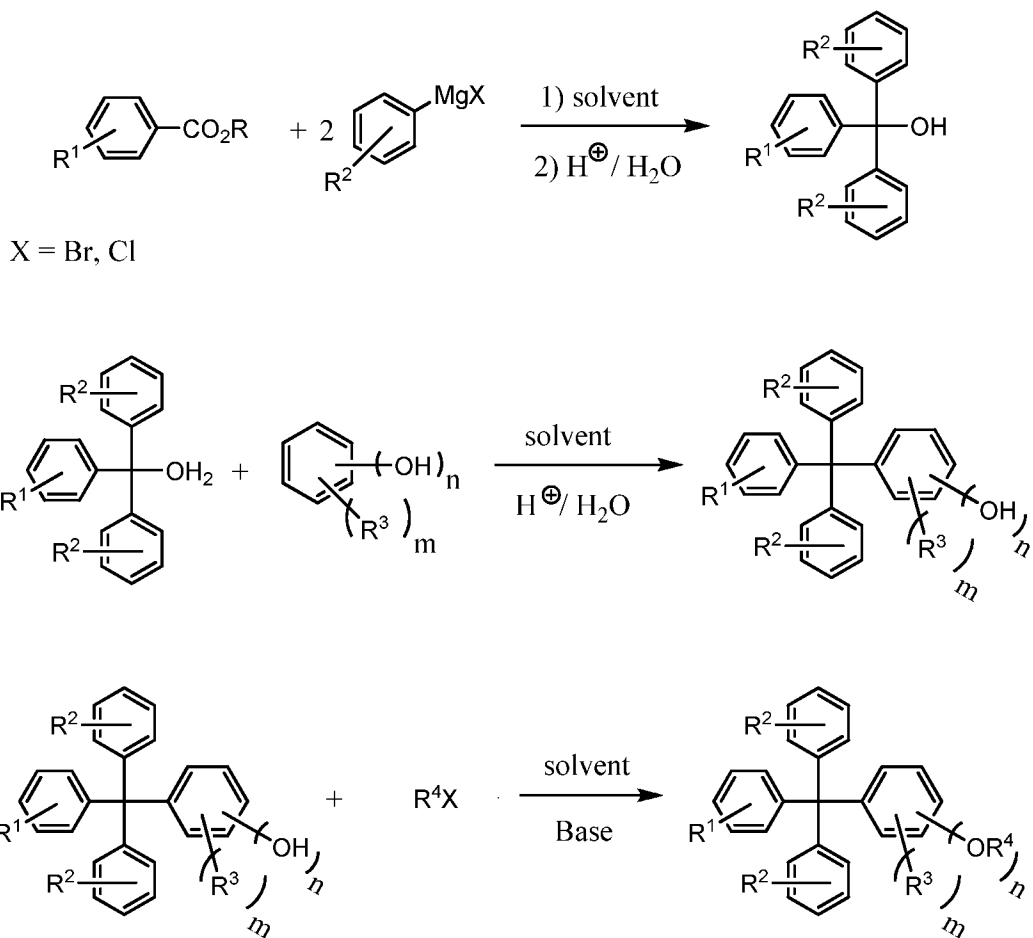
Preferably, the marker compounds have a log P value of at least 3, where P is the 1-octanol/water partition coefficient. Preferably, the marker compounds have a log P of at least 4, preferably at least 5. Log P values which have not been experimentally determined and reported in the literature can be estimated using the method disclosed in Meylan, W.M & Howard, P.H., *J. Pharm. Sci.*, vol. 84, pp. 83-92 (1995). Preferably the petroleum hydrocarbon or liquid biologically derived fuel is a petroleum hydrocarbon, biodiesel fuel or ethanol fuel; preferably a petroleum hydrocarbon or biodiesel fuel; preferably a petroleum hydrocarbon; preferably crude oil, gasoline, diesel fuel, kerosene, jet fuel or heating oil; preferably gasoline.

Preferably, the marker compounds are detected by at least partially separating them from constituents of the petroleum hydrocarbon or liquid biologically derived fuel using a chromatographic technique, e.g., gas chromatography, liquid chromatography, thin-layer chromatography, paper chromatography, adsorption chromatography, affinity chromatography, capillary electrophoresis, ion exchange and molecular exclusion chromatography. Chromatography is followed by at least one of: (i) mass spectral analysis, and (ii) FTIR. Identities of the marker compounds preferably are determined by mass spectral analysis. Preferably, mass spectral analysis is used to detect the marker compounds

in the petroleum hydrocarbon or liquid biologically derived fuel without performing any separation. Alternatively, marker compounds may be concentrated prior to analysis, e.g., by distilling some of the more volatile components of a petroleum hydrocarbon or liquid biologically derived fuel.

5            Preferably, more than one marker compound is present. Use of multiple marker compounds facilitates incorporation into the petroleum hydrocarbon or liquid biologically derived fuel of coded information that may be used to identify the origin and other characteristics of the petroleum hydrocarbon or liquid biologically derived fuel. The code comprises the identities and relative amounts, e.g., fixed integer ratios, of the marker  
10            compounds. One, two, three or more marker compounds may be used to form the code. Marker compounds according to this invention may be combined with markers of other types, e.g., markers detected by absorption spectrometry, including those disclosed in U.S. Pat. No. 6,811,575; U.S. Pat. App. Pub. No. 2004/0250469 and EP App. Pub. No. 1,479,749. Marker compounds are placed in the petroleum hydrocarbon or liquid biologically derived fuel  
15            directly, or alternatively, placed in an additives package containing other compounds, e.g., antiwear additives for lubricants, detergents for gasoline, etc., and the additives package is added to the petroleum hydrocarbon or liquid biologically derived fuel.

            The compounds of this invention may be prepared by methods known in the art, e.g., reaction of substituted esters with aryl Grignard reagents and arylation with substituted  
20            phenols, followed by alkylation with organic halides in the presence of base. For example, tritylated phenolic ethers may be prepared according to the following reaction scheme, in which, for simplicity, j, p and r are one and k, q and s are zero. All other symbols are as defined above. Products having more complicated substitution patterns can be made from the corresponding starting materials using the same process. In an alternative synthesis, a  
25            substituted or unsubstituted benzophenone is allowed to react with a substituted or unsubstituted phenyl Grignard reagent to produce the trityl alkyl phenol, which then reacts with  $R^4X$ .



## EXAMPLES

Common laboratory reagents and solvents were obtained from Sigma-Aldrich, Fluka, VWR, Acros, or Fisher Scientific, and were used as received. The benzoic acid esters, Grignard reagents and the phenols were obtained from Sigma-Aldrich.

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### ANALYSIS PROCEDURES

IR Analyses: IR analyses were performed using a Nicolet 560 FTIR spectrometer. For liquid samples, a small drop was cast as a neat film between two KBr plates. The IR spectrum was acquired in the transmission mode from 4000 to 400  $\text{cm}^{-1}$ , with a spectral resolution of 4  $\text{cm}^{-1}$ . A Happ-Genzel type apodization function was used.

10

NMR Analyses: Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were acquired using a Bruker 200 NMR spectrometer operating at 4.7 T.  $^1\text{H}$  spectra were obtained using an 8.2 second accumulation time and 2.0 KHz sweep width; the  $^{13}\text{C}$  spectra were obtained at a 4.7 second accumulation time and 7.0 KHz sweep width. Methanol- $\text{d}_4$  was typically used as the solvent. Chemical shifts were referenced using the solvent resonances at 3.30 ppm for  $^1\text{H}$ , and at 59.05 ppm for  $^{13}\text{C}$ .

15

GPC ANALYSES: GPC analyses to follow the progress of synthesis reactions and to determine product purity were performed using a PerkinElmer Series 200 HPLC. Two Polymer Laboratories  $\mu\text{L}$ gel columns were used in series: 1) 300 mm x 7.5 mm, 3 $\mu$ , 100  $\text{\AA}$ ; 2) 300 mm x 7.5 mm, 5 $\mu$ , 50  $\text{\AA}$ . These two columns are preceded by a guard column. The columns are maintained at 35 $^\circ\text{C}$ . The mobile phase is 100% THF at a flow rate of 2 mL / minute. UV detection is at 270 nm. The program run time is 10 minutes.

20

GC ANALYSES: GC analyses to follow the progress of synthesis reactions and to determine product purity were performed using a Hewlett Packard Model 6890N gas chromatograph with FID detector. The column was a Thermo Scientific TR5, 7 meter x 0.32 mm x 0.25  $\mu\text{m}$  film. The run program started with the oven at 50 $^\circ\text{C}$  with an initial hold time of 1 minute, followed by a temperature ramp up to 280 $^\circ\text{C}$  at 10 $^\circ\text{C}$  / minute, and a final hold time of 20 minutes. The injection port temperature and detector temperatures were both 275 $^\circ\text{C}$ . The sample injection size was 1  $\mu\text{L}$ , and the carrier gas was helium at 1 mL / minute.

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Melting Points: Melting points were determined using a Mel-Temp apparatus, and were uncorrected.



## SYNTHESIS OF ALKYL TRITYL ALCOHOLS

General Synthesis Procedure: The following example is representative of the procedure used for the synthesis of all of the alkyl trityl alcohols. Synthesis data are summarized in Table 1 below.

5            Phenyldi-m-tolylmethanol [95938-57-1] (mmMTritOH): A 500 mL 4-neck flask was equipped with a magnetic stir bar, a 60 mL addition funnel, and 4 glass stoppers. The equipment was dried overnight in a 125°C oven. Upon removal from the oven, the equipment was quickly assembled and was cooled to room temperature under a stream of nitrogen. The flask was charged with 200 mL of 1.0M m-tolyl magnesium chloride in THF  
10 (0.2 moles). The addition funnel was charged with 13.63 grams (0.1 mole) of methyl benzoate in 30 mL of dry THF. Under a nitrogen blanket, the methyl benzoate solution was added to the stirred Grignard solution dropwise over a period of about 2.5 hours. During the addition, the Grignard solution turned from a yellow-brown to a violet color. Shortly after the addition began, an exotherm to about 37°C was observed. The addition rate was adjusted  
15 to keep the reaction mixture temperature at or below this temperature. After the addition was completed, the reaction mixture temperature was increased to 60°C for 2.5 hours. The reaction mixture was then stirred at room temperature for several days. GC analysis of a sample of the reaction mixture showed the presence of unreacted benzoate ester. The reaction mixture was re-heated to 60 – 65°C, monitoring the formation of product by GC  
20 analysis. After about 10 hours, the amount of unreacted ester was slightly more than 2 area %, and the amount of mmMTritOH was > 85 area %. The reaction mixture was poured onto a mixture of 100 mL of 10 volume % sulfuric acid in water and about 300 grams of ice. About 100 mL of ether was added, and the mixture was stirred until the ice melted. The mixture was transferred to a separatory funnel, and the layers were separated. The aqueous  
25 layer was extracted with 1 x 50 mL of ether, and the ether layers were combined. The combined ether layers were washed with 2 x 50 mL of saturated aqueous sodium bicarbonate solution and then with 2 x 50 mL of saturated aqueous sodium chloride solution. The ether solution was dried over anhydrous magnesium sulfate, then it was filtered and the solvent was removed by rotary evaporation to give 26.33 grams of mmMTritOH as a viscous amber  
30 oil. Yield = 91.3 %. Product purity by GC analysis was > 91 area %. Product structure was confirmed by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR, and GC/MS analyses.

## SYNTHESIS OF ALKYL TRITYL PHENOLS

General Synthesis Procedure: The following example is representative of the procedure used for the synthesis of all of the alkyl trityl phenols. Synthesis data are summarized in Table 2 below.

5                    2-(sec-Butyl)-4-(diphenyl)(p-tolyl)methylphenol (pMS4): A 100 mL 3-neck flask was equipped with a magnetic stirrer and a reflux condenser with nitrogen blanket. The flask was charged with 6.86 grams (0.025 moles) of diphenyl(p-tolyl)methanol (pMTritOH; [5440-76-6]), with 3.76 grams (0.025 moles) of o-sec-butylphenol, and with 50 mL of glacial acetic acid. The mixture was stirred under nitrogen at room temperature to give a clear  
10 yellow solution. To this solution were added 5 mL of concentrated sulfuric acid. The clear yellow acetic acid solution immediately turned deep red brown. The reaction mixture was stirred at room temperature, monitoring reaction progress by GPC analysis. After 6 days, the amount of remaining unreacted o-sec-butylphenol had decreased to about 7 area %, and the amount of mMS4 present had increased to about 83 area %. The reaction mixture was  
15 poured into about 250 mL of water and about 150 mL of toluene were added. The mixture was stirred at room temperature for about 1 hour, then the mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with 1 x 50 mL of toluene, and the toluene layers were combined. The toluene solution was washed with 1 x 100 mL of water, and with 1 x 100 mL of saturated aqueous sodium chloride  
20 solution. The toluene solution was dried over anhydrous magnesium sulfate, then it was filtered and the solvent was removed by rotary evaporation to give 10 grams of pMS4 as a viscous dark red oil. Yield was 100 %; product purity by GPC analysis was 82 area %. Product structure was confirmed by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR, and GC/MS analyses.

## 25 SYNTHESIS OF ALKYL TRITYL PHENYL ETHERS

General Synthesis Procedure: The following example is representative of the procedure used for the synthesis of all of the alkyl trityl phenyl ethers. Synthesis data are summarized in Table 3 below.

30                    ((3,4-Bis(hexyloxy)phenyl)(p-tolyl)methylene)dibenzene (pM3,4-6): A 100 mL 3-neck flask was equipped with a magnetic stirrer, a reflux condenser with nitrogen blanket, and a heating mantle with a temperature controller and a thermocouple. The flask was charged with 3.67 grams (0.01 mole) of 4-(diphenyl(p-tolyl)methyl)benzene-1,2-diol (pM3,4), 1.41 grams (0.21 moles) of 85 % potassium hydroxide pellets, and with 25 mL of

dimethyl sulfoxide. The mixture was stirred under nitrogen and was heated to 105°C. Heating and stirring were continued until all of the potassium hydroxide pellets were dissolved. A dark red brown solution was obtained. The reaction mixture was cooled to 55°C, and 3.30 grams (0.02 moles) of bromohexane were added in one portion. As exotherm  
5 to 66°C was observed. The reaction mixture was then maintained at 65°C and was monitored by GC analysis. After 2 hours, almost no pM3,4 remained. The reaction mixture was poured into about 250 mL of water containing a few pellets of potassium hydroxide and several grams of sodium chloride. About 150 mL of toluene were added, and the mixture was stirred at room temperature for about 1 hour. The mixture was transferred to a separatory funnel and  
10 the layers were separated. The aqueous layer was extracted with 1 x 50 mL of toluene, and the toluene layers were combined. The toluene solution was washed with 1 x 75 mL of saturated aqueous sodium chloride solution, and was then dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation to give 3.80 grams of pM3,4-6 as a dark red oil. Yield was 71 %. Purity was > 90 area % by GC. Product structure was  
15 confirmed by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR, and GC/MS analyses.

#### CANDIDATE ASSESSMENT STUDIES

GC/MS Studies: Stock solutions of alkyl trityl phenyl ether candidate were prepared in dichloromethane (DCM). These DCM solutions were used to establish GC retention times  
20 and MS fragmentation patterns. A summary of GC retention times and MS fragmentation data are summarized in Table 4 below.

##### GC/MS Parameters:

- Column: Agilent DB 35m, 15.0 m X 0.25 mm X 0.25 μ
- Flow Rate: 1.5 mL / min. He carrier gas
- 25 - Oven: initial: 100°C
- Ramp 1: 20°C / min. to 280°C; Hold: 10 min.
- Ramp 2: 20°C / min. to 340°C; Hold: 6 min.
- Inlet Temp.: 280°C
- Inset: Splitless; Vent: 15 min., Single taper, glass wool, deactivated, 5062-3587
- 30 - Injection Volume: 3 μL; Viscosity: 5 sec., Plunger: fast
- Mass Transfer Line Temp.: 280°C
- MS Quad: 200°C; MS Source: 250°C
- Solvent Delay: 18.5 min.

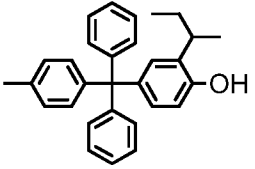
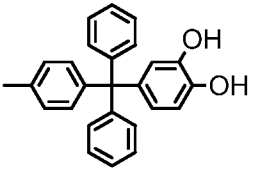
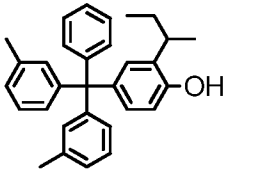
Solubility Studies: The solubility properties of the alkyl trityl phenyl ethers were determined by mixing 0.1 grams of test sample with 0.9 grams of solvent. The mixtures were warmed to 60°C for a few minutes to make homogeneous solutions. The solutions were cooled back to room temperature, and then they were placed into a freezer at -10°C. The solutions were checked daily to see if crystallization had occurred. The solvents evaluated were ADVASOL 200H (mixed aromatics solvent from Advanced Aromatics), ADVASOL 200H ND (naphthalene-depleted mixed aromatics solvent from Advanced Aromatics), cyclohexanone, and o-sec-butyl phenol (OSBP). Solubility data results are summarized in Table 5 below.

Assessment Summary: The GC retention time, GC/MS fragmentation and solubility performance results of the alkyl trityl phenyl ethers were all favorable for application as fuel markers.

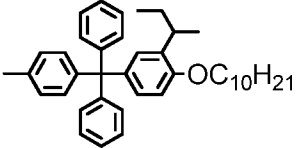
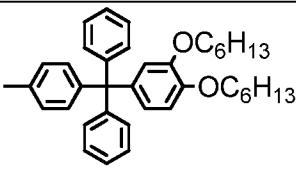
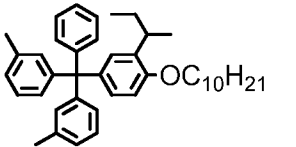
TABLE 1: Synthesis Data for Alkyl Trityl Alcohols

<u>STRUCTURE</u>	<u>Designation</u>	<u>M.W.</u>	<u>% Yield</u>	<u>GC Area % Purity</u>	<u>mp, °C</u>
	pMTritOH	274.36	92.2	96.4	78 – 79
	mmMTritOH	288.38	90	> 91	oil
	ommMTritOH	302.41	88.5	> 51	oil

TABLE 2: Synthesis Data for Alkyl Trityl Phenols

<u>STRUCTURE</u>	<u>Designation</u>	<u>M.W.</u>	<u>% yield</u>	<u>GPC (GC)</u> <u>Area %</u> <u>Purity</u>	<u>mp, °C</u>
	pMS4	406.56	100	82	oil
	pM3,4	366.45	55	89	175 - 180
	mmMS4	420.59	78	(75)	oil

5 TABLE 3: Synthesis Data for Alkyl Trityl Phenyl Ethers

<u>STRUCTURE</u>	<u>Designation</u>	<u>M.W.</u>	<u>% yield</u>	<u>GPC (GC)</u> <u>Area %</u> <u>Purity</u>	<u>mp, °C</u>
	pMS4-10	546.82	89	(> 75)	oil
	pM3,4-6	534.77	71	> 90	oil
	mmMS4-10	560.40	79.6	(70)	oil

**TABLE 4:** Summary of GC Retention Time and GC/MS Fragmentation Data for Alkyl Trityl Phenyl Ethers

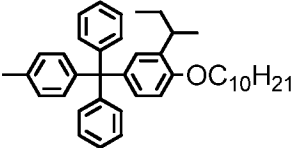
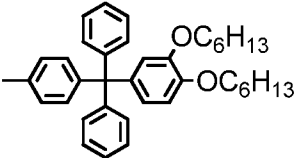
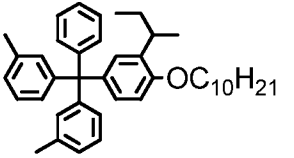
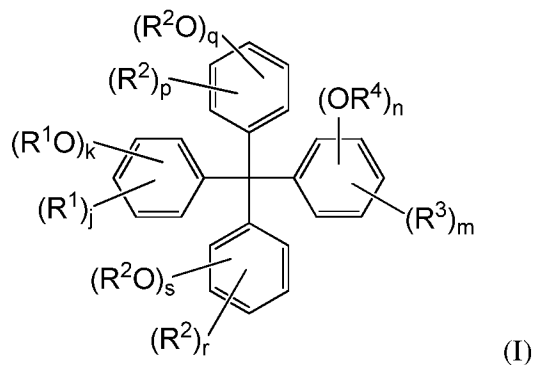
<u>STRUCTURE</u>	<u>DESIGNATION</u>	<u>M.W.</u>	<u>GC Retention Time, Min.</u>	<u>GC/MS Major Ion Masses, m/e</u>
	pMS4-10	546.82	22.24	546, 469
	pM3,4-6	534.77	22.89	534, 457, 373
	mmMS4-10	560.40	21.69	560, 469

TABLE 5: Solubility Data Summary for Alkyl Trityl Phenyl Ethers

<u>Alkyl Trityl Phenyl Ether</u>	<u>WT. % Alkyl Trityl Phenyl Ether</u>	<u>SOLVENT SYSTEM</u>	<u>Solubility at -10°C, Days</u>
pMS4-10	10	200H – OSBP (75:25, w:w)	Soluble after 7 days
		200H ND – OSBP (75:25, w:w)	Soluble after 7 days
		200H	Soluble after 7 days
		200H ND	Soluble after 7 days
		200H – cyclohexanone (75:25, w:w)	Soluble after 7 days
		200H ND – cyclohexanone (75:25, w:w)	Soluble after 7 days
pM3,4-6	10	200H – OSBP (75:25, w:w)	Soluble after 76 days
		200H ND – OSBP (75:25, w:w)	Soluble after 76 days
		200H	Soluble after 18 days; crystals after 35 days
		200H ND	Soluble after 18 days; crystals after 35 days
		200H – cyclohexanone (75:25, w:w)	Soluble after 7 days
		200H ND – cyclohexanone (75:25, w:w)	Soluble after 7 days
mmMS4-10	10	200H – OSBP (75:25, w:w)	Soluble after 102 days
		200H – cyclohexanone (75:25, w:w)	Soluble after 102 days

## CLAIMS

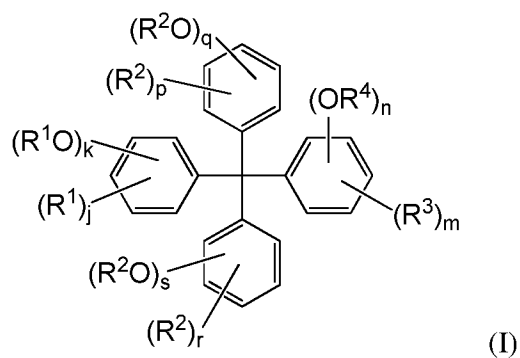
1. A compound having formula (I)



wherein  $R^1$  and  $R^2$  independently represent  $C_1$ - $C_6$  alkyl;  $R^3$  is  $C_1$ - $C_6$  alkyl;  $R^4$  is  $C_1$ - $C_{18}$  alkyl or  $C_4$ - $C_{18}$  heteroalkyl;  $m$  is zero, one, two or three;  $n$  is one, two or three; and  $j$ ,  $k$ ,  $p$ ,  $q$ ,  $r$  and  $s$  independently are zero, one or two; provided that at least one of  $j$ ,  $k$ ,  $p$ ,  $q$ ,  $r$  and  $s$  is not zero.

2. The compound of claim 1 in which  $n$  is one or two;  $m$  is zero or one;  $j$ ,  $p$  and  $r$  are zero or one; and  $k$ ,  $q$  and  $s$  are zero.
3. The compound of claim 2 in which  $R^4$  is  $C_2$ - $C_{12}$  saturated alkyl.
4. The compound of claim 3 in which  $R^1$  and  $R^2$  independently represent hydrogen or  $C_1$ - $C_4$  alkyl.
5. The compound of claim 4 in which  $R^3$  is  $C_3$ - $C_6$  alkyl.
6. A method for marking a petroleum hydrocarbon or a liquid biologically derived fuel; said method comprising adding to said petroleum hydrocarbon or liquid biologically derived fuel at least one compound having formula (I)





wherein  $R^1$  and  $R^2$  independently represent  $C_1$ - $C_6$  alkyl;  $R^3$  is  $C_1$ - $C_6$  alkyl;  $R^4$  is  $C_1$ - $C_{18}$  alkyl or  $C_4$ - $C_{18}$  heteroalkyl;  $m$  is zero, one, two or three;  $n$  is one, two or three; and  $j$ ,  $k$ ,  $p$ ,  $q$ ,  $r$  and  $s$  independently are zero, one or two; provided that at least one of  $j$ ,  $k$ ,  $p$ ,  $q$ ,  $r$  and  $s$  is not zero; and wherein each compound having formula (I) is present at a level from 0.01 ppm to 20 ppm.

7. The method of claim 6 in which  $n$  is one or two;  $m$  is zero or one;  $j$ ,  $p$  and  $r$  are zero or one; and  $k$ ,  $q$  and  $s$  are zero..

8. The method of claim 7 in which  $R^4$  is  $C_2$ - $C_{12}$  saturated alkyl.

9. The method of claim 8 in which  $R^1$  and  $R^2$  independently represent hydrogen or  $C_1$ - $C_4$  alkyl.

10. The method of claim 9 in which  $R^3$  is  $C_3$ - $C_6$  alkyl.

INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2014/033004

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. C07C43/205  
 ADD. C07C39/14 C07C33/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 EPO-Internal, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; ISHII, YASUO ET AL: "Polyester compositions for products with high strength and good processability and dyeingability", XP002726695, retrieved from STN Database accession no. 1994:219598 abstract & JP 6 041399 A (KAO CORP, JAPAN) 15 February 1994 (1994-02-15) ----- -/--	1

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search  4 July 2014	Date of mailing of the international search report  16/07/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Watchorn, Peter
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## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/033004

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA [Online]            CHEMICAL ABSTRACTS SERVICE, COLUMBUS,            OHIO, US;            PAILLON-JEGOU, DENISE ET AL: "Reaction of            aromatic compounds with some amins and            the corresponding aldehydes",            XP002726696,            retrieved from STN            Database accession no. 1979:103560            abstract            &amp; PAILLON-JEGOU, DENISE ET AL: "Reaction            of aromatic compounds with some amins            and the corresponding aldehydes",            BULLETIN DE LA SOCIETE CHIMIQUE DE FRANCE            , (5-6, PT. 2), 234-40 CODEN: BSCFAS;            ISSN: 0037-8968,            1978,</p>	1
X	<p>-----            DATABASE CA [Online]            CHEMICAL ABSTRACTS SERVICE, COLUMBUS,            OHIO, US;            ZHOU, BING ET AL: "Synthesis of alkyl aryl            ethers under cesium carbonate catalyzed            O-alkylation of phenol",            XP002726697,            retrieved from STN            Database accession no. 2007:511654            abstract            &amp; ZHOU, BING ET AL: "Synthesis of alkyl            aryl ethers under cesium carbonate            catalyzed O-alkylation of phenol",            HUNAN DAXUE XUEBAO, ZIRAN KEXUEBAN ,            34(3), 64-66 CODEN: HDAXE3,            2007,</p>	1-4
X	<p>-----            DATABASE CA [Online]            CHEMICAL ABSTRACTS SERVICE, COLUMBUS,            OHIO, US;            XU, XINHUA ET AL: "Method for preparing            alkyl aryl ether with Cs<sub>2</sub>CO<sub>3</sub> as catalyst            in acetonitrile as solvent.",            XP002726698,            retrieved from STN            Database accession no. 2007:1064929            abstract            &amp; CN 101 037 381 A (HUNAN UNIVERSITY,            PEOP. REP. CHINA)            19 September 2007 (2007-09-19)            -----            -/--</p>	1-4

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International application No  
PCT/US2014/033004

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MICHAEL MASTALERZ ET AL: "Synthesis of Tetrahedral Shape-Persistent Tetranuclear Metal-salphens", EUROPEAN JOURNAL OF ORGANIC CHEMISTRY, vol. 2011, no. 30, 25 October 2011 (2011-10-25), pages 5971-5980, XP55126938, ISSN: 1434-193X, DOI: 10.1002/ejoc.201100745 page 5972; compound 2 -----	1
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X	WO 2012/177987 A1 (ANGUS CHEMICAL [US]; GREEN GEORGE D [US]; SWEDO RAYMOND [US]) 27 December 2012 (2012-12-27) page 1, paragraph 1-2 page 9; table 1 -----	1-10
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X,P	WO 2014/008164 A1 (ANGUS CHEMICAL [US]; ROHM & HAAS [US]) 9 January 2014 (2014-01-09) page 1, paragraph 1-2 page 10 - page 11; table 3 -----	1-10

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Information on patent family members

International application No

PCT/US2014/033004

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