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(54) Title: TRITYLATED ETHERS

(57) Abstract: A compound having formula $(\text{Ph}_3\text{C})_m\text{Ar}(\text{OR})_n$, wherein Ph represents a phenyl group, Ar is an aromatic ring system having from six to twenty carbon atoms, R is $\text{C}_1\text{-C}_{18}$ alkyl or $\text{C}_7\text{-C}_{12}$ aralkyl, m is one or two, and n is an integer from one to four.



WO 2012/177987 A1

TRITYLATED 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 $(\text{Ph}_3\text{C})_m\text{Ar}(\text{OR})_n$, wherein Ph represents a phenyl group, Ar is an aromatic ring system having from six to twenty carbon atoms, R is $\text{C}_1\text{-C}_{18}$ alkyl or $\text{C}_7\text{-C}_{12}$ aralkyl, m is one or two, and n is an integer from one to four.

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 $(\text{Ph}_3\text{C})_m\text{Ar}(\text{OR})_n$, wherein Ph represents a phenyl group, Ar is an aromatic ring system having from six to twenty carbon atoms, R is $\text{C}_1\text{-C}_{18}$ alkyl or $\text{C}_7\text{-C}_{12}$ aralkyl, m is one or two, and n is an integer from one to four.

DETAILED DESCRIPTION

Percentages are weight percentages (wt%) and temperatures are in °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

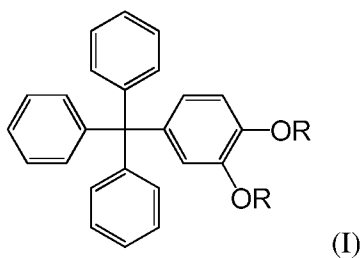
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oxygen, nitrogen, sulfur or phosphorus; petroleum hydrocarbons include crude oils as well as products derived from petroleum refining processes; they include, for example, crude oil, lubricating oil, hydraulic fluid, brake fluid, gasoline, diesel fuel, kerosene, jet fuel and heating oil. Marker compounds of this invention can be added to a petroleum hydrocarbon or
5 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°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
10 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 or branched arrangement. Substitution on alkyl groups of one or more hydroxy or alkoxy groups is permitted. Preferably, alkyl groups are saturated and unsubstituted. An "aryl" group is a substituent
15 derived from an aromatic hydrocarbon compound. An aryl group has a total of from six to twenty ring atoms, unless otherwise specified, and has one or more rings which are separate or fused. Substitution on aryl groups of one or more alkyl or alkoxy groups is permitted. An "aralkyl" group is an "alkyl" group substituted by an "aryl" group. Preferably, the compounds of this invention contain elements in their naturally occurring isotopic
20 proportions.

Ar is an aromatic ring system having from six to twenty carbon atoms and whose substituents include Ph₃C and OR groups, preferably one in which the only substituents are Ph₃C and OR groups. Preferably, Ar is a C₆-C₁₂ hydrocarbyl aromatic ring system. Preferably, Ar is benzene, naphthalene, biphenyl, phenyl ether, diphenylmethane or one of
25 the preceding systems substituted with alkyl and/or alkoxy groups; preferably benzene. Preferably, n is from one to three, preferably two or three, preferably two. Preferably, R is C₁-C₁₈ alkyl or C₇-C₁₀ aralkyl, preferably C₂-C₁₆ alkyl or C₇-C₉ aralkyl, preferably C₃-C₁₂ alkyl or C₇-C₉ aralkyl, preferably C₂-C₁₆ alkyl, preferably C₂-C₁₂ alkyl, preferably C₃-C₁₂ alkyl, preferably C₃-C₁₀ alkyl.

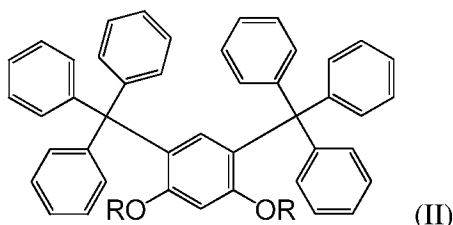
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Preferably, the compound of this invention is represented by formula (I)



wherein R is C₁-C₁₈ alkyl, preferably C₂-C₁₈ alkyl, preferably C₂-C₁₆ alkyl, preferably C₂-C₁₂ alkyl, preferably C₃-C₁₂ alkyl, preferably C₃-C₁₀ alkyl.

Preferably, the compound of this invention is represented by formula (II)



5 wherein R is C₁-C₁₈ alkyl, preferably C₂-C₁₈ alkyl, preferably C₂-C₁₆ alkyl, preferably C₂-C₁₂ alkyl, preferably C₃-C₁₂ alkyl, preferably C₃-C₁₀ alkyl.

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.

10 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.

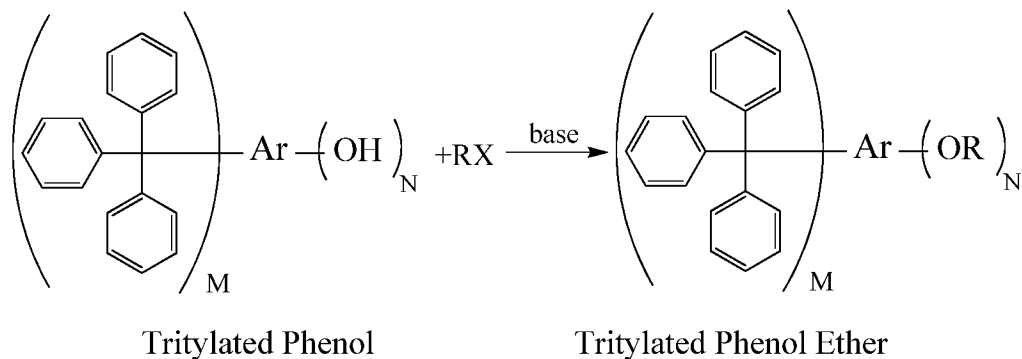
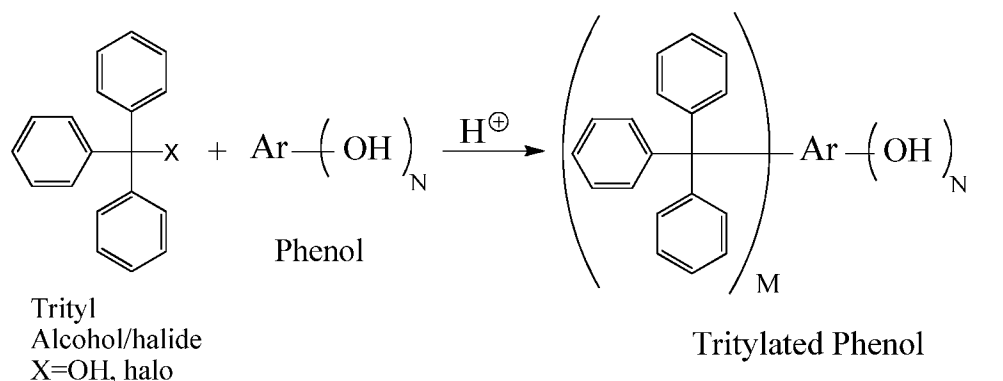
Preferably, the marker compounds have a log P value of at least 3, where P is the 1-octanol/water partition coefficient. Preferably, the marker compounds have a log P of at least 4, preferably at least 5. Log P values which have not been experimentally determined and reported in the literature can be 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.

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 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

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.,
 5 alkylation of phenols or polyhydroxyaromatics with trityl halide or alcohol, 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,



10 wherein M is one or two and N is 1 to 4.

EXAMPLES

Typical mono-tritylated phenol synthesis procedure is illustrated by the following example:

5 4-Tritylbenzene-1,2-diol [6331-97-1] (TritCatp): A 1L 3-neck flask was equipped with a mechanical stirrer, a reflux condenser with nitrogen blanket, and a heating mantle with a temperature controller and a thermocouple. The flask was charged with 78.20 grams (0.30 moles) of trityl alcohol, 39.39 grams (0.36 moles) of catechol, and 250 mL of glacial acetic acid. The mixture was stirred under nitrogen while heating to about 80°C. A clear amber solution was obtained. To this solution were added 16.73 grams (0.06 moles) of trityl
10 chloride in one portion. The chloride dissolved quickly. The mixture was brought to reflux. After about 30 minutes at reflux, solids began to separate out. Reflux was continued for another 5 hours before cooling to room temperature. The reaction mixture was filtered, and the grey solids were washed on the filter with several portions of acetic acid. The product was dried – first in air and finally in a vacuum oven at 60°C for 2 hours. The yield of product
15 was 92.0 grams (72.5%), having a melting point of 245 – 248°C. The structure was confirmed by IR, ¹H- and ¹³C-NMR, and GC/MS analyses.

Typical bis-tritylated phenol synthesis procedure is illustrated by the following example:

20 4,6-Ditrylbenzene-1,3-diol (Bis-Trit-Res): A 1L 3-neck flask was equipped with a mechanical stirrer, a reflux condenser with nitrogen blanket, and a heating mantle with a temperature controller and a thermocouple. The flask was charged with 12.39 grams (0.0475 moles) of trityl alcohol, 15.03 grams (0.054 moles) of trityl chloride, 5.53 grams (0.05 moles) of resorcinol, and with 50 mL of glacial acetic acid. The mixture was stirred under nitrogen
25 while heating to reflux. At about 80°C, a clear amber solution was obtained. Solids began to separate out after about 30 minutes. Reflux was continued for a total of about 34 hours. The reaction mixture was cooled to room temperature, then it was filtered. The white solids were washed on the filter with several portions of acetic acid. The product was dried – first in air for about 2 hours, and then in a vacuum oven at 50°C for 3 hours. The yield of product was
30 15.27 grams (95%), having a melting point of 272 – 274°C. The structure was confirmed by IR, ¹H- and ¹³C-NMR, and GC/MS analyses.

Typical mono-tritylated phenol ether synthesis procedure is illustrated by the following example:

5 ((3,4-Bis(hexyloxy)phenyl)methanetryl)tribenzene (BHex-TCatp): 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 3.52 grams (0.01 moles) of 4-tritylbenzene-1,2-diol, 1.32 grams (0.02 moles, 85 wt. %) of potassium hydroxide pellets, and with 25 mL of dimethylsulfoxide. The mixture was stirred
10 under nitrogen while heating to 105°C. After about 20 minutes, all of the potassium hydroxide had dissolved, and the mixture was cooled to 70°C. 1-Bromohexane (3.30 grams, 0.02 moles) was then added in one portion. An exotherm to about 88°C was observed. After the exotherm subsided, the reaction mixture was maintained at 75°C for about 1.5 hours. A sample withdrawn for GPC analysis at this point showed no remaining tritylated phenol,
15 indicating that the reaction was completed. The reaction mixture was cooled to <50°C and was poured into 500 mL of water. Solids precipitated. After stirring at room temperature for about 1.5 hours, the mixture was filtered, and the beige solids were washed on the filter with several portions of water, then they were air-dried. The yield of product was 3.35 grams (64%), having a melting point of 75 – 77°C. The structure was confirmed by IR, ¹H- and ¹³C-
20 NMR, and GC/MS analyses.

The filtrate from above was milky, and contained additional product which could have been isolated by extraction. In those cases in which, upon quenching the reaction mixture in water, the product separated as an oil, extraction with ethyl ether was used in place of filtration.

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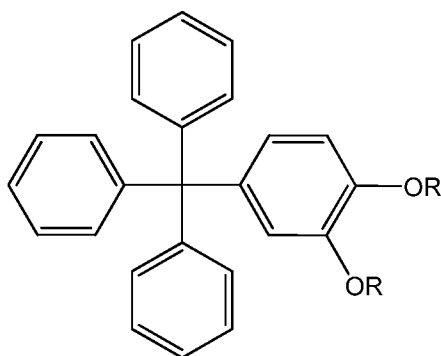
Typical bis-tritylated phenol ether synthesis procedure is illustrated by the following example:

((4,6-Bis(hexyloxy)-1,3-phenylene)bis(methanetryl))hexabenzene (BHex-BTRes): A 100
30 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 5.95 grams (0.01 moles) of 4,6-ditrylbenzene-1,3-diol (Bis-Trit-Res), 1.32 grams (0.02 moles, 85 wt. %) of potassium hydroxide pellets, and with 25 mL of

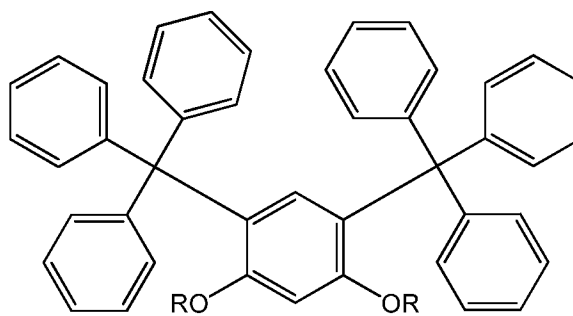
dimethylsulfoxide. The mixture was stirred under nitrogen while heating to 105°C. After about 20 minutes, all of the potassium hydroxide had dissolved, and the mixture was cooled to 70°C. 1-Bromohexane (3.30 grams, 0.02 moles) was then added in one portion. An exotherm to about 88°C was observed. After the exotherm subsided, the reaction mixture was maintained at 75°C for about 1.5 hours. A sample withdrawn for GPC analysis at this point showed no remaining tritylated phenol, indicating that the reaction was completed. The reaction mixture was cooled to <50°C and was poured into 500 mL of water. Solids precipitated. After stirring at room temperature for about 1.5 hours, the mixture was filtered, and the beige solids were washed on the filter with several portions of water, then they were air-dried. The yield of product was 4.37 grams (84%), having a melting point of 164 – 166°C. The structure was confirmed by IR, ¹H- and ¹³C-NMR, and GC/MS analyses.

Using the above procedure, the following tritylated catechol ethers were prepared:

15



Mono-tritylated
catechol ethers



Bis-tritylated
resorcinol ethers

TABLE 1: Synthesis Data for Tritylated Catechol Ethers

<u>Mono-Tritylated Catechol Ethers: R=</u>	<u>% Yield</u>	<u>MP, °C</u>
n-C ₄ H ₉	77.4	79 – 80.5
n-C ₅ H ₁₁	92.5	(oil)
n-C ₆ H ₁₃	64	75 – 77
n-C ₇ H ₁₅	88	67 – 69
n-C ₈ H ₁₇	79.7	58 – 62
<u>Bis-Tritylated Resorcinol Ethers: R=</u>	<u>% Yield</u>	<u>MP, °C</u>
n-C ₆ H ₁₃	94	272 - 274

TABLE 2: Stability and Extractability* data for Fuel Marker Candidate BHex-TCatp

5

Sample	Marker Area %	Internal Standard area % C30	ratio	Marker %	Change %
std sample	292845	347044	0.84	100.00	0.00
5 % NaOH	284966	347629	0.82	97.15	-2.85
50 % NaOH	300708	354885	0.85	100.42	0.42
5 % H ₂ SO ₄	300688	353739	0.85	100.73	0.73
98 % H ₂ SO ₄	166305	362121	0.46	54.43	-45.57
2 % Charcoal	294103	347771	0.85	100.22	0.22
5 % bleach	295119	349006	0.85	100.21	0.21
2% Metal specs	288374	346719	0.83	98.57	-1.43

* Test Protocols: 2000 mg/kg solution with internal standard was made in xylenes, then dosed with 5 % by weight of 5% NaOH, 50 % NaOH, 5 % sulfuric acid and 98% sulfuric acid. It was also tested with 2 % charcoal 5 % bleach and 2 % metal specs by wt/wt.

GC Sensitivity and Repeatability Data for BHex-TCatp

Method Evaluation for BHex-TCatp in Diesel 2:

Stock	Stock(mg/ml)	SubStock(ug/ml)
BHex-TCatp	0.26	5.11

6.39mg in 25 ml DCM, 0.5 ml Stock in 25 ml Diesel

Standard	1	2	3	4	5
Substock (ul)	200	400	600	800	1000
BHex-TCatp(ug/L)	102	204	307	409	511

5

Linearity and Accuracy:

Standard	Conc(ppb)	Area (520+443)	Conc.(ppb)	% Recovery
1	102	52537	101.9	99.7
1	102	50989	98.9	96.7
2	204	102479	198.5	97.1
2	204	107034	207.3	101.4
3	307	159596	309.0	100.7
3	307	161848	313.4	102.2
4	409	213638	413.5	101.1
4	409	212133	410.6	100.4
5	511	263991	511.0	100.0
5	511	259911	503.1	98.4

Repeatability and Accuracy:

Concentration	307ppb			
Rep	Area	Conc.(ppb)	%Recovery	
1	155936	301.9	98.4	
2	155981	302.0	98.5	
3	157936	305.8	99.7	
4	157497	304.9	99.4	
5	152073	294.5	96.0	
6	157354	304.7	99.3	
Avg.	156130	302.3	98.6	
Std Dev	2152	4.16	1.36	
RSD	1.38	1.38	1.38	

Notes:

1. SIM: 520+443
2. Solvent: commercial diesel fuel
3. Method:
 - AGILENT DB-35 - 15 meter x 0.25mm x 0.25 μ m
 - sample size = 3 μ L
 - flow rate = 1.5 mL / min
 - initial temp = 100 C
 - rate 1 = 20 C / min
 - final temp 1 = 280 C
 - hold = 10 min
 - rate 2 = 20 C / min
 - final temp 2 = 340 C
 - hold = 6 min
 - inlet temp = 280 C

Oven: 100-20C/min-280(10)-20C/min-340(4), 3 μ l,

Viscosity delay: 1sec.

Solvent delay: 18min

Split open: 16min

Plotting Area (y) against concentration (x) from the linearity data above gave a straight line with equation $y=516.9259x + 135.9$, with $R^2=0.9991$.

CLAIMS

1. A compound having formula $(\text{Ph}_3\text{C})_m\text{Ar}(\text{OR})_n$, wherein Ph represents a phenyl group, Ar is an aromatic ring system having from six to twenty carbon atoms, R is $\text{C}_1\text{-C}_{18}$ alkyl or $\text{C}_7\text{-C}_{12}$ aralkyl, m is one or two, and n is an integer from one to four.
2. The compound of claim 1 in which Ar is a $\text{C}_6\text{-C}_{12}$ hydrocarbyl aromatic ring system.
3. The compound of claim 2 in which n is an integer from one to three.
4. The compound of claim 3 in which R is $\text{C}_2\text{-C}_{18}$ alkyl.
5. The compound of claim 4 in which Ar is a benzene ring system, n is two, and R is $\text{C}_3\text{-C}_{12}$ 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 $(\text{Ph}_3\text{C})_m\text{Ar}(\text{OR})_n$, wherein Ph represents a phenyl group, Ar is an aromatic ring system having from six to twenty carbon atoms, R is $\text{C}_1\text{-C}_{18}$ alkyl or $\text{C}_7\text{-C}_{10}$ aralkyl, m is one or two, and n is an integer from one to four, wherein each compound having formula $(\text{Ph}_3\text{C})_m\text{Ar}(\text{OR})_n$ is present at a level from 0.01 ppm to 20 ppm.
7. The method of claim 6 in which Ar is a $\text{C}_6\text{-C}_{12}$ hydrocarbyl aromatic ring system.
8. The method of claim 7 in which n is an integer from one to three.
9. The method of claim 8 in which R is $\text{C}_2\text{-C}_{18}$ alkyl.
10. The method of claim 9 in which Ar is a benzene ring system, n is two, and R is $\text{C}_3\text{-C}_{12}$ alkyl.

INTERNATIONAL SEARCH REPORT

International application No PCT/US2012/043718

A. CLASSIFICATION OF SUBJECT MATTER INV. C10L1/185 C07C43/20 C10M129/16 C10M171/00 C10L1/00 ADD.				
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) C10L C07C C10M				
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, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	NESTOR BARROETA ET AL: THE JOURNAL OF ORGANIC CHEMISTRY, vol. 31, no. 7, 1 July 1966 (1966-07-01), pages 2330-2333, XP55036219, ISSN: 0022-3263, DOI: 10.1021/jo01345a059 page 2332, column 2; figures 1, 2 page 2333, column 1 -----	1-5		
X	GABRIEL CHUCHANI ET AL: THE JOURNAL OF ORGANIC CHEMISTRY, vol. 31, no. 5, 1 May 1966 (1966-05-01), pages 1573-1576, XP55036134, ISSN: 0022-3263, DOI: 10.1021/jo01343a061 page 1575, column 2 ----- ----- -/--	1-4		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.</td> <td style="width: 50%; border: none;"><input checked="" type="checkbox"/> See patent family annex.</td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.			
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"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search	Date of mailing of the international search report			
29 August 2012	06/09/2012			
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 de La Morinerie, B			

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/043718

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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