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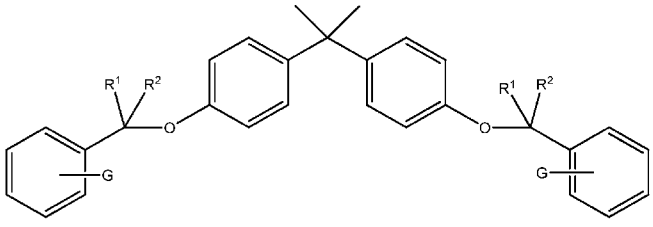
(54) Title: BISPHENOL A COMPOUNDS AS MARKERS FOR LIQUID HYDROCARBONS AND OTHER FUELS AND OILS



(I)

(57) Abstract: A method for marking a petroleum hydrocarbon or a liquid biologically derived fuel by adding at least one compound having formula (I), wherein R^1 and R^2 independently represent hydrogen or C_1-C_4 alkyl groups, and G represents hydrogen or at least one substituent selected from the group consisting of C_1-C_{18} alkyl and C_1-C_{18} alkoxy.

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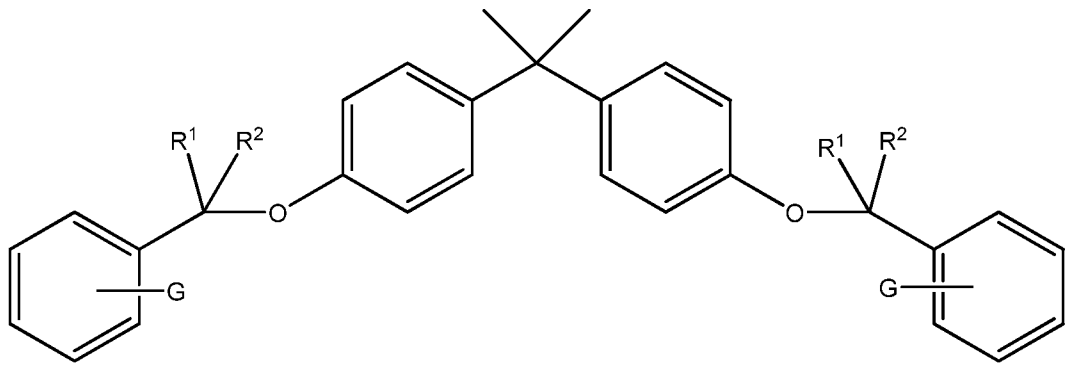
BISPHENOL A COMPOUNDS AS MARKERS FOR LIQUID HYDROCARBONS AND OTHER FUELS AND OILS

This invention relates to a method for marking liquid hydrocarbons and other fuels and oils with suitable compounds.

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.

STATEMENT OF INVENTION

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



(I)

wherein R^1 and R^2 independently represent hydrogen or C_1-C_4 alkyl groups, and G represents hydrogen or at least one substituent selected from the group consisting of C_1-C_{18} alkyl and C_1-C_{18} alkoxy.

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 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°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 or branched arrangement. An "alkyl" group may have double or triple bonds. Substitution on alkyl groups of one or more hydroxy or alkoxy groups is permitted. Preferably, alkyl groups are saturated and unsubstituted. Preferably, the compounds of this invention contain elements in their naturally occurring isotopic proportions.

G represents hydrogen or at least one substituent selected from the group consisting of C_1-C_{18} alkyl and C_1-C_{18} alkoxy, i.e., each aromatic ring bearing a "G" substituent in formula (I) is unsubstituted or has at least one substituent selected from the group consisting of C_1-C_{18} alkyl and C_1-C_{18} alkoxy. Preferably, when G is not hydrogen it represents one to three substituents on each aromatic ring, which may be the same or different, preferably one or two substituents, preferably two or three substituents, preferably two or three identical substituents. However, the substituents represented by "G" are the same on the two aromatic rings substituted by G,. i.e., the compound is symmetric with a plane of symmetry between the benzene rings of the central biphenyl moiety. Preferably, G represents hydrogen or at least one substituent selected from the group consisting of C_1-C_{12} alkyl and C_1-C_{12} alkoxy, preferably C_1-C_8 alkyl and C_1-C_8 alkoxy, preferably C_1-C_6 alkyl and C_1-C_6 alkoxy, preferably

C_1-C_4 alkyl and C_1-C_4 alkoxy, preferably C_1-C_4 alkyl, preferably C_1-C_3 alkyl, preferably methyl and ethyl. Preferably, R^1 and R^2 independently represent hydrogen, methyl or ethyl; preferably hydrogen or methyl. Preferably, R^1 is methyl and R^2 is hydrogen, preferably R^1 and R^2 both are hydrogen. Preferably, G does not represent hydrogen. Preferably, G does not represent a single substituent in the 4-position. Preferably, when R^1 and R^2 represent hydrogen, G represents at least one saturated alkyl group, preferably not in the 4-position.

In the method of this invention, preferably the minimum amount of each marker 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.

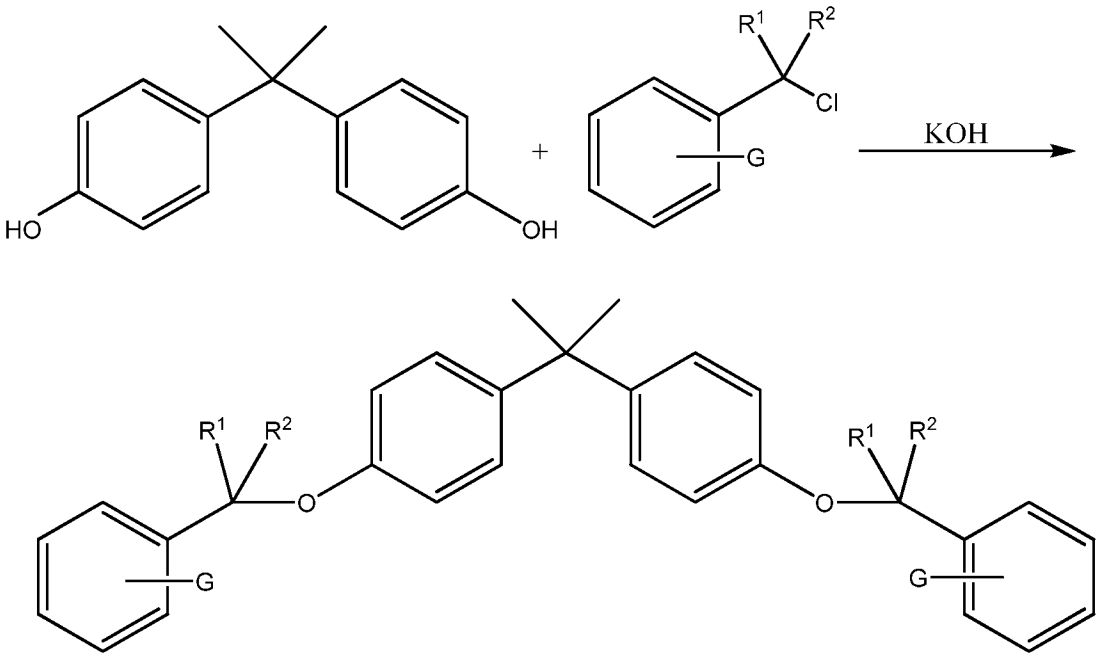
Preferably, the marker compounds have a log P value of at least 3, where P is the 1-octanol/water partition coefficient. Preferably, the marker compounds have a log P of at least 4, preferably at least 5. Log P values which have not been experimentally determined and reported in the literature can be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

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. For example, substituted benzyl halides may react with Bisphenol A in the presence of base according to the following equation


HO
OH
+
R1
R2
Cl
G
KOH
R1
R2
O
G
R1
R2
O
G

EXAMPLES

Example 1: Preparation of Bisphenol A bis(2-methylbenzyl) ether:

Under an inert atmosphere, 5.23 g Bisphenol A (BPA) (22.9 mmol) and 2.83 g potassium hydroxide (50.4 mmol) were dissolved in 50 mL dimethylacetamide. Stirring was started at 500 rpm and the contents were warmed to 70 °C. After 30 minutes, 7.09 g 2-methylbenzyl chloride (50.4 mmol) dissolved in 50 mL dimethylacetamide was added to the reaction mixture. The mixture was then heated at 100 °C for 4 h until no 2-methylbenzyl chloride was noted in the GPC trace. During the course of the reaction, a white precipitate had formed. The reaction mixture was cooled to room temperature and then poured into a 1 L separatory funnel containing 200 mL deionized water. The aqueous layer immediately became opaque. The reaction flask was washed with 50 mL deionized water and this wash was added along with 150 mL toluene to the separatory funnel. The separatory funnel was shaken and the bilayer allowed to settle. The lower, aqueous layer appeared opaque while the upper, organic layer was clear and colorless. The organic layer was separated and the aqueous layer was washed 3 additional times with 100 mL toluene. The combined organic fractions were dried over 20 g magnesium sulfate and filtered into a 1 L round bottom flask. The solvent was removed from the filtered toluene solution on a rotary evaporator initially at room temperature then at 70 °C. Following solvent removal, a viscous oil remained in the round bottom flask. This crude product was recrystallized at 0 °C from an acetone solution. The crystalline white solid that had formed was filtered on a 7.0 cm Büchner funnel using Whatman 540 filter paper. The crystals were pulverized into a powder and washed with cold acetone. The white powder was transferred to a 75 °C vacuum oven and dried for 24 h. For Bisphenol A bis(2-methylbenzyl) ether: 52 % yield (5.2 g, 12 mmol); white powder; mp 117 °C. ^{1}H NMR (500.1 MHz, CD_2Cl_2, ppm, J = Hz): 7.40 (d, 7.2, 2H, Ph), 7.23 (m, 6H, Ph), 7.17 (m, 4H, Ph), 6.90 (m, 4H, Ph), 5.02 (s, 4H, -PhC$\underline{H}_2$O-), 2.37 (s, 6H, -PhC$\underline{H}_3$), 1.65 (s, 6H, -C(C$\underline{H}_3$)$_2$).

Example 2: Preparation of Bisphenol A bis(3-methylbenzyl) ether:

Prepared according to the procedure of Example 1 from BPA and 3-methylbenzyl chloride - 21 % yield; colorless oil. ^{1}H NMR (500.1 MHz, CD_2Cl_2, ppm, J = Hz): 7.22 – 7.29 (m, 6H, Ph), 7.15 (m, 6H, Ph), 6.87 (m, 4H, Ph), 5.00 (s, 4H, -PhC$\underline{H}_2$O-), 2.37 (s, 6H, -PhC$\underline{H}_3$), 1.64 (s, 6H, -C(C$\underline{H}_3$)$_2$).

Example 3: Preparation of Bisphenol A bis(4-methylbenzyl) ether (composition known, CAS# 87353-49-9):

Prepared according to the procedure of Example 1 from BPA and 4-methylbenzyl chloride - 61 % yield; white powder; mp 101 °C. ^{1}H NMR (500.1 MHz, CD_2Cl_2, ppm, J = Hz): 7.32 (d, 8.1, 4H, Ph), 7.20 (d, 7.9, 4H, Ph), 7.15 (m, 4H, Ph), 6.87 (m, 4H, Ph), 4.99 (s, 4H, -PhC$\underline{H}_2$O-), 2.36 (s, 6H, -PhC$\underline{H}_3$), 1.64 (s, 6H, -C(C$\underline{H}_3$)$_2$).

Example 4: Preparation of Bisphenol A bis(alpha-methylbenzyl) ether:

Prepared according to the procedure of Example 1 from BPA and alpha-methylbenzyl chloride - 84 % yield; gold oil. ^{1}H NMR (500.1 MHZ, $(CD_3)_2CO$, ppm, J = Hz): 7.42 (m, 4H, Ph), 7.33 (m, 4H, Ph), 7.24 (m, 2H, Ph), 7.01 (m, 4H, Ph), 6.76 (m, 4H, Ph), 5.39 (q, 6.5, 2H, PhC$\underline{H}$(Me)O-), 1.52 – 1.57 (m, 12H, Me).

Example 5: Demonstration of GC-MS detectability

Method Evaluation for Ex. 1 Product in DCM:

Stock	Stock(mg/ml)	SubStock(µg/ml)
Ex. 1 product	1.13	11.300

11.3mg in 10 ml DCM, 0.25 ml Stock in 25ml DCM

Standard	1	2	3	4
Substock	200µl	400µl	600µl	800µl
Ex. 1 product (µg/L)	226	452	678	904

Linearity and Accuracy:

Standard	**Conc(ppb)**	**Area**	**Conc.(ppb)**	**%Recovery**
1	226	48058	239.8	106.1
1	226	47839	239.1	105.8
2	452	114210	445.2	98.5
2	452	110243	432.9	95.8
3	678	186029	668.3	98.6
3	678	183055	659.0	97.2
4	904	264936	913.3	101.0
4	904	267871	922.4	102.0

Plotting area against concentration gave a line with slope=321.9825, intercept= -29140 and R^2=0.9968

Repeatability and Accuracy:

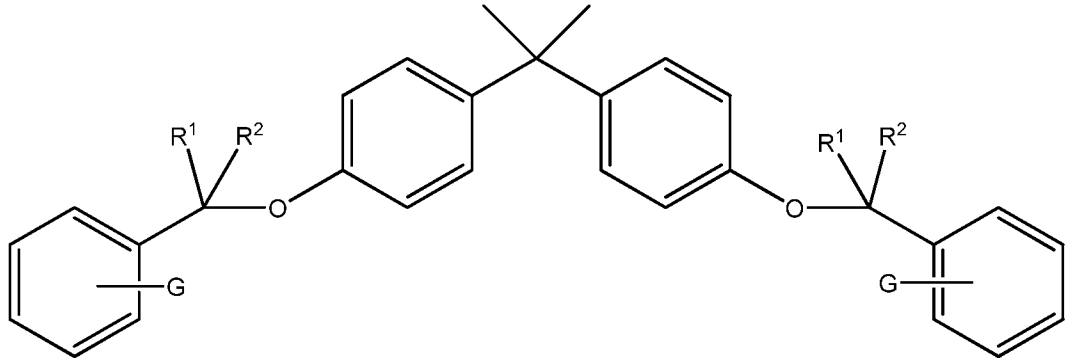
Concentration	226ppb		
Rep	Area	Conc.(ppb)	%Recovery
1	41152	218.3	96.6
2	42116	221.3	97.9
3	45887	233.0	103.1
4	48805	242.1	107.1
5	48058	239.8	106.1
6	47839	239.1	105.8
Avg.	45643	232.3	102.8
Std Dev	3266	10.14	4.49
RSD	7.15	4.37	4.37

Note: 1. SIM: 105

2. Solvent: Dichloromethane (DCM)

CLAIMS

1. 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),



(I)

wherein R^1 and R^2 independently represent hydrogen or C_1-C_4 alkyl groups, and G represents hydrogen or at least one substituent selected from the group consisting of C_1-C_{18} alkyl and C_1-C_{18} alkoxy.

2. The method of claim 1 in which each compound of formula (I) is present at a level from 0.01 ppm to 20 ppm.

3. The method of claim 2 in which R^1 and R^2 represent hydrogen or methyl.

4. The method of claim 3 in which G represents hydrogen or at least one substituent selected from the group consisting of C_1-C_8 alkyl and C_1-C_8 alkoxy.

5. The method of claim 4 in which R^1 and R^2 represent hydrogen.

6. The method of claim 5 in which each compound of formula (I) is present at a level from 0.01 ppm to 10 ppm.

7. The method of claim 6 in which G represents hydrogen or one or two substituents selected from the group consisting of C_1-C_6 alkyl and C_1-C_6 alkoxy.

8. The method of claim 7 in which said petroleum hydrocarbon or liquid biologically derived fuel is a petroleum hydrocarbon, biodiesel fuel or ethanol fuel.

9. The method of claim 8 in which G represents one or two substituents selected from the group consisting of C_1-C_4 alkyl and C_1-C_4 alkoxy.

10. The method of claim 9 in which G represents one or two substituents selected from the group consisting of methyl and ethyl, and each compound of formula (I) is present at a level from 0.02 ppm to 8 ppm.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/043108

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L1/22
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

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, 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.
A	US 2007/184555 A1 (BANAVALI RAJIV MANOHAR [US] ET AL) 9 August 2007 (2007-08-09) cited in the application the whole document -----	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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"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
3 September 2012	17/09/2012

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2012/043108

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007184555 A1	09-08-2007	AT 513894 T	15-07-2011
		BR PI0700223 A	06-11-2007
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