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(12) **United States Patent**
Kanj et al.

(10) **Patent No.:** **US 9,447,682 B2**

(45) **Date of Patent:** **Sep. 20, 2016**

(54) **CARBON-BASED FLUORESCENT TRACERS AS OIL RESERVOIR NANO-AGENTS**

(2013.01); *B82Y 20/00* (2013.01); *C09K 2211/10* (2013.01); *Y10S 977/774* (2013.01); *Y10S 977/95* (2013.01)

(71) Applicants: **SAUDI ARABIAN OIL COMPANY**, Dhahran (SA); **CORNELL UNIVERSITY**, Ithaca, NY (US)

(58) **Field of Classification Search**
None
See application file for complete search history.

(72) Inventors: **Mazen Y. Kanj**, Dhahran (SA); **Mohammad Harunar Rashid**, Ithaca, NY (US); **Emmanuel Giannelis**, Ithaca, NY (US)

(56) **References Cited**

U.S. PATENT DOCUMENTS

7,505,131 B2 3/2009 Roth
7,712,528 B2 5/2010 Langdon et al.
7,770,646 B2 8/2010 Klassen et al.
7,782,460 B2 8/2010 Difoggio et al.
7,829,772 B2 11/2010 Sun
7,907,277 B2 3/2011 Csutak

(Continued)

FOREIGN PATENT DOCUMENTS

WO 2007050984 A2 5/2007

OTHER PUBLICATIONS

Shelia N. Baker et al., "Luminescent Carbon Nanodots: Emergent Nanolights", *Angewandte Chemie*, (2010), pp. 6726-6744, vol. 49, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, www.angewandte.org.

(Continued)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/627,688**

(22) Filed: **Feb. 20, 2015**

(65) **Prior Publication Data**

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Related U.S. Application Data

(62) Division of application No. 13/469,459, filed on May 11, 2012.

(60) Provisional application No. 61/486,090, filed on May 13, 2011.

(51) **Int. Cl.**

E21B 49/00 (2006.01)
C09K 11/06 (2006.01)
C07C 235/74 (2006.01)
C09K 11/65 (2006.01)
B82Y 20/00 (2011.01)

(52) **U.S. Cl.**

CPC **E21B 49/008** (2013.01); **C07C 235/74** (2013.01); **C09K 11/06** (2013.01); **C09K 11/65**

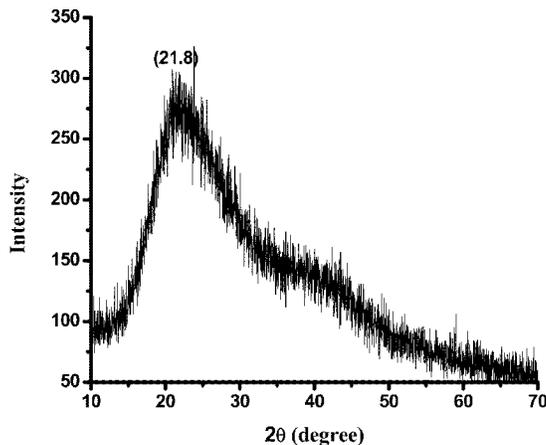
Primary Examiner — Jeffrey Washville

(74) *Attorney, Agent, or Firm* — Bracewell LLP; Constance G. Rhebergen; Brian H. Tompkins

(57) **ABSTRACT**

The present invention relates to carbon-based fluorescent nano-agent tracers for analysis of oil reservoirs. The carbon-based fluorescent nano-agents may be used in the analysis of the porosity of a formation. The nanoagents are suitable for injection into a petroleum reservoir and may be recovered from the reservoir for the determination of hydrocarbon flow rates and retention times.

12 Claims, 13 Drawing Sheets





US009453159B2

(12) **United States Patent**
Kanj et al.

(10) **Patent No.:** **US 9,453,159 B2**

(45) **Date of Patent:** **Sep. 27, 2016**

(54) **CARBON-BASED FLUORESCENT TRACERS AS OIL RESERVOIR NANO-AGENTS**

(56) **References Cited**

(71) Applicants: **SAUDI ARABIAN OIL COMPANY**, Dhahran (SA); **CORNELL UNIVERSITY**, Ithaca, NY (US)

(72) Inventors: **Mazen Y. Kanj**, Dhahran (SA); **Mohammad Harunar Rashid**, Ithaca, NY (US); **Emmanuel Giannelis**, Ithaca, NY (US)

(73) Assignees: **Saudi Arabian Oil Company**, Dhahran (SA); **Cornell University**, Ithaca, NY (US)

U.S. PATENT DOCUMENTS

7,505,131	B2	3/2009	Roth	
7,712,528	B2	5/2010	Langdon et al.	
7,770,646	B2	8/2010	Klassen et al.	
7,782,460	B2	8/2010	Difoggio et al.	
7,829,772	B2	11/2010	Sun	
7,907,277	B2	3/2011	Csutak	
2001/0018503	A1	8/2001	Whipple et al.	
2010/0125035	A1	5/2010	Zhang et al.	
2010/0148049	A1	6/2010	Csutak	
2010/0240900	A1	9/2010	Zhang et al.	
2010/0268470	A1	10/2010	Kamal et al.	
2011/0151576	A1	6/2011	Perfect et al.	
2012/0318503	A1*	12/2012	Kanj	C09K 9/02 166/252.6

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

FOREIGN PATENT DOCUMENTS

WO 2007050984 A2 5/2007

(21) Appl. No.: **14/627,522**

(22) Filed: **Feb. 20, 2015**

(65) **Prior Publication Data**

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Related U.S. Application Data

(62) Division of application No. 13/469,459, filed on May 11, 2012.

(60) Provisional application No. 61/486,090, filed on May 13, 2011.

(51) **Int. Cl.**
C09K 11/06 (2006.01)

(52) **U.S. Cl.**
CPC **C09K 11/06** (2013.01); **C09K 2211/10** (2013.01)

(58) **Field of Classification Search**
None
See application file for complete search history.

OTHER PUBLICATIONS

Shelia N. Baker et al., "Luminescent Carbon Nanodots: Emergent Nanolights", *Angewandte Chemie*, (2010), pp. 6726-6744, vol. 49, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, www.angewandte.org.

(Continued)

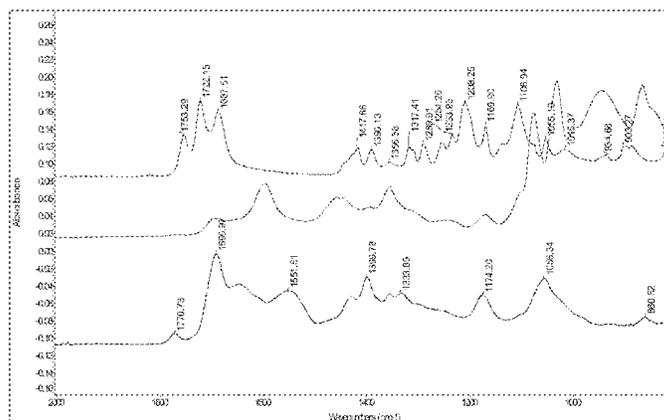
Primary Examiner — Jeffrey Washville

(74) *Attorney, Agent, or Firm* — Bracewell LLP; Constance G. Rhebergen; Brian H. Tompkins

(57) **ABSTRACT**

The present invention relates to carbon-based fluorescent nano-agent tracers for analysis of oil reservoirs. The carbon-based fluorescent nano-agents may be used in the analysis of the porosity of a formation. The nanoagents are suitable for injection into a petroleum reservoir and may be recovered from the reservoir for the determination of hydrocarbon flow rates and retention times.

8 Claims, 13 Drawing Sheets





US009464034B2

(12) **United States Patent**
Kanj et al.

(10) **Patent No.:** **US 9,464,034 B2**

(45) **Date of Patent:** **Oct. 11, 2016**

(54) **CARBON-BASED FLUORESCENT TRACERS AS OIL RESERVOIR NANO-AGENTS**

(75) Inventors: **Mazen Y. Kanj**, Dhahran (SA);
Mohammad Harunar Rashid, Assam (IN); **Emmanuel Giannelis**, Ithaca, NY (US)

(73) Assignees: **Saudi Arabian Oil Company**, Dhahran (SA); **Cornell University**, Ithaca, NY (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 965 days.

(21) Appl. No.: **13/469,459**

(22) Filed: **May 11, 2012**

(65) **Prior Publication Data**

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Related U.S. Application Data

(60) Provisional application No. 61/486,090, filed on May 13, 2011.

(51) **Int. Cl.**

C07C 233/00 (2006.01)
E21B 49/00 (2006.01)
C07C 231/00 (2006.01)
B82Y 35/00 (2011.01)
C07C 227/18 (2006.01)
C09K 9/02 (2006.01)

(52) **U.S. Cl.**

CPC **C07C 227/18** (2013.01); **C09K 9/02** (2013.01); **C09K 2208/10** (2013.01); **Y10T 428/2982** (2015.01)

(58) **Field of Classification Search**

None
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

7,505,131 B2	3/2009	Roth	
7,597,959 B2 *	10/2009	Wang	C08F 297/02 428/403
7,712,528 B2	5/2010	Langdon et al.	
7,770,646 B2	8/2010	Klassen et al.	
7,782,460 B2	8/2010	DiFoggio et al.	
7,829,772 B2	11/2010	Sun	
7,907,277 B2	3/2011	Csutak	
2001/0018503 A1	8/2001	Whipple et al.	
2008/0113448 A1 *	5/2008	Sun	436/501
2010/0125035 A1	5/2010	Zhang et al.	
2010/0148049 A1	6/2010	Csutak	
2010/0215760 A1 *	8/2010	Kundu	A61K 9/5115 424/499
2010/0240900 A1	9/2010	Zhang et al.	

(Continued)

FOREIGN PATENT DOCUMENTS

WO 2007050984 A2 5/2007

OTHER PUBLICATIONS

International Search Report and Written Opinion Issued in PCT Application No. PCT/US2012/037419, Issued May 11, 2012 (11 pages).

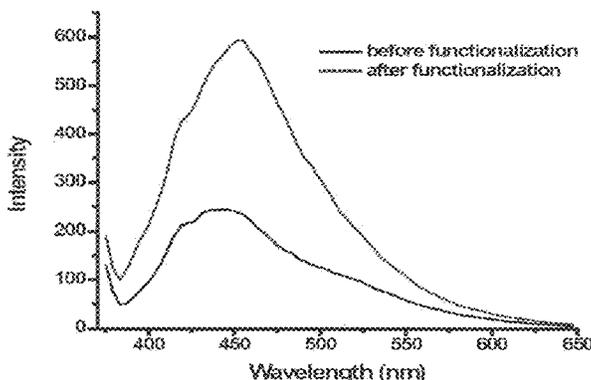
(Continued)

Primary Examiner — Jeffrey Washville
(74) *Attorney, Agent, or Firm* — Bracewell LLP;
Constance G. Rhebergen; Brian H. Tompkins

(57) **ABSTRACT**

Carbon-based fluorescent nano-agent tracers for analysis of oil reservoirs are provided. The carbon-based fluorescent nano-agents being inexpensive means of analyzing, among other properties, the porosity of a formation. The nanoagents are suitable for injection into a petroleum reservoir and can be subsequently recovered for determinations of flow rates and retention times.

12 Claims, 13 Drawing Sheets





US009469599B2

(12) **United States Patent**
Kanj et al.

(10) **Patent No.:** **US 9,469,599 B2**

(45) **Date of Patent:** **Oct. 18, 2016**

(54) **CARBON-BASED FLUORESCENT TRACERS AS OIL RESERVOIR NANO-AGENTS**

(56) **References Cited**

U.S. PATENT DOCUMENTS

(71) Applicants: **SAUDI ARABIAN OIL COMPANY**, Dhahran (SA); **CORNELL UNIVERSITY**, Ithaca, NY (US)

7,505,131	B2	3/2009	Roth	
7,712,528	B2	5/2010	Langdon et al.	
7,770,646	B2	8/2010	Klassen et al.	
7,782,460	B2	8/2010	Difoggio et al.	
7,829,772	B2	11/2010	Sun	
7,907,277	B2	3/2011	Csutak	
2001/0018503	A1	8/2001	Whipple et al.	
2005/0050656	A1*	3/2005	Huang	A61K 8/64 8/406

(72) Inventors: **Mazen Y. Kanj**, Dhahran (SA); **Mohammad Harunar Rashid**, Ithaca, NY (US); **Emmanuel Giannelis**, Ithaca, NY (US)

(73) Assignees: **Saudi Arabian Oil Company**, Dhahran (SA); **Cornell University**, Ithaca, NY (US)

2010/0125035	A1	5/2010	Zhang et al.	
2010/0148049	A1	6/2010	Csutak	
2010/0240900	A1	9/2010	Zhang et al.	

(Continued)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

FOREIGN PATENT DOCUMENTS

WO	2007050984	A2	5/2007
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(21) Appl. No.: **14/627,613**

OTHER PUBLICATIONS

(22) Filed: **Feb. 20, 2015**

Shelia N. Baker et al., "Luminescent Carbon Nanodots: Emergent Nanolights", *Angewandte Chemie*, (2010), pp. 6726-6744, vol. 49, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, www.angewandte.org.

(65) **Prior Publication Data**

US 2015/0239826 A1 Aug. 27, 2015

(Continued)

Related U.S. Application Data

(62) Division of application No. 13/469,459, filed on May 11, 2012.

Primary Examiner — Jeffrey Washville

(60) Provisional application No. 61/486,090, filed on May 13, 2011.

(74) *Attorney, Agent, or Firm* — Bracewell LLP; Constance G. Rhebergen; Brian H. Tompkins

(51) **Int. Cl.**

C07C 227/18 (2006.01)

C09K 9/02 (2006.01)

(52) **U.S. Cl.**

CPC **C07C 227/18** (2013.01); **C09K 9/02** (2013.01); **C09K 2208/10** (2013.01); **Y10T 428/2982** (2015.01)

(57) **ABSTRACT**

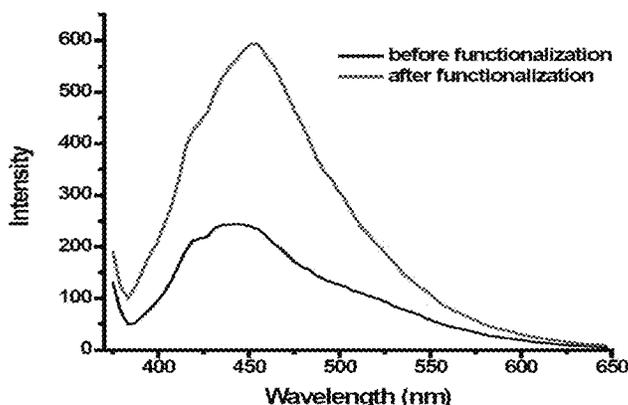
The present invention relates to carbon-based fluorescent nano-agent tracers for analysis of oil reservoirs. The carbon-based fluorescent nano-agents may be used in the analysis of the porosity of a formation. The nanoagents are suitable for injection into a petroleum reservoir and may be recovered from the reservoir for the determination of hydrocarbon flow rates and retention times.

(58) **Field of Classification Search**

None

See application file for complete search history.

9 Claims, 13 Drawing Sheets





US009493700B2

(12) **United States Patent**
Kanj et al.

(10) **Patent No.:** **US 9,493,700 B2**

(45) **Date of Patent:** **Nov. 15, 2016**

(54) **CARBON-BASED FLUORESCENT TRACERS AS OIL RESERVOIR NANO-AGENTS**

(71) Applicants: **SAUDI ARABIAN OIL COMPANY**, Dhahran (SA); **CORNELL UNIVERSITY**, Ithaca, NY (US)

(72) Inventors: **Mazen Y. Kanj**, Dhahran (SA); **Mohammad Harunar Rashid**, Ithaca, NY (US); **Emmanuel Giannelis**, Ithaca, NY (US)

(73) Assignees: **Saudi Arabian Oil Company**, Dhahran (SA); **Cornell Univeristy**, Ithaca, NY (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/627,776**

(22) Filed: **Feb. 20, 2015**

(65) **Prior Publication Data**
US 2015/0232748 A1 Aug. 20, 2015

Related U.S. Application Data

(62) Division of application No. 13/469,459, filed on May 11, 2012.

(60) Provisional application No. 61/486,090, filed on May 13, 2011.

(51) **Int. Cl.**
C07C 233/00 (2006.01)
E21B 49/00 (2006.01)
C07C 231/00 (2006.01)
B82Y 35/00 (2011.01)
C09K 11/06 (2006.01)
C09K 11/65 (2006.01)
C07H 15/04 (2006.01)
B82Y 20/00 (2011.01)

(52) **U.S. Cl.**
CPC **C09K 11/06** (2013.01); **C07H 15/04** (2013.01); **C09K 11/65** (2013.01); **E21B 49/00** (2013.01); **B82Y 20/00** (2013.01); **C09K 2211/10** (2013.01); **Y10S 977/774** (2013.01); **Y10S 977/95** (2013.01)

(58) **Field of Classification Search**
None
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,271,307 A * 9/1966 Dickson et al. 166/280.1
3,292,696 A * 12/1966 Sandiford 166/400
4,659,676 A * 4/1987 Rhyne, Jr. 436/56
7,505,131 B2 3/2009 Roth

(Continued)

FOREIGN PATENT DOCUMENTS

WO 2007050984 A2 5/2007

OTHER PUBLICATIONS

Institute for Energy Technology: "New functional tracers based on nanotechnology and radiotracer generators" Strategic Institute Programme 2007-2009, Sep. 17, 2007.*

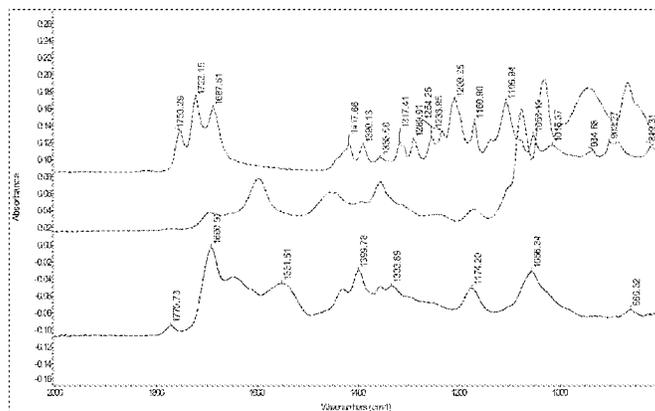
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Primary Examiner — Jeffrey Washville
(74) *Attorney, Agent, or Firm* — Bracewell LLP;
Constance G. Rhebergen; Brian H. Tompkins

(57) **ABSTRACT**

The present invention relates to carbon-based fluorescent nano-agent tracers for analysis of oil reservoirs. The carbon-based fluorescent nano-agents may be used in the analysis of the porosity of a formation. The nanoagents are suitable for injection into a petroleum reservoir and may be recovered from the reservoir for the determination of hydrocarbon flow rates and retention times.

13 Claims, 13 Drawing Sheets





US009528045B2

(12) **United States Patent**
Kanj et al.

(10) **Patent No.:** **US 9,528,045 B2**

(45) **Date of Patent:** **Dec. 27, 2016**

(54) **CARBON-BASED FLUORESCENT TRACERS AS OIL RESERVOIR NANO-AGENTS**

(2013.01); *C09K 2211/10* (2013.01); *Y10S 977/774* (2013.01); *Y10S 977/95* (2013.01); *Y10T 428/2982* (2015.01)

(71) Applicants: **SAUDI ARABIAN OIL COMPANY**, Dhahran (SA); **CORNELL UNIVERSITY**, Ithaca, NY (US)

(58) **Field of Classification Search**
None
See application file for complete search history.

(72) Inventors: **Mazen Y. Kanj**, Dhahran (SA); **Mohammad Harunar Rashid**, Ithaca, NY (US); **Emmanuel Giannelis**, Ithaca, NY (US)

(56) **References Cited**

U.S. PATENT DOCUMENTS

7,505,131 B2 3/2009 Roth
7,712,528 B2 5/2010 Langdon et al.
7,770,646 B2 8/2010 Klassen et al.
7,782,460 B2 8/2010 Difoggio et al.
7,829,772 B2 11/2010 Sun

(Continued)

(73) Assignees: **Saudi Arabian Oil Company**, Dhahran (SA); **Cornell University**, Ithaca, NY (US)

FOREIGN PATENT DOCUMENTS

WO 2007050984 A2 5/2007

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

OTHER PUBLICATIONS

Shelia N. Baker et al., "Luminescent Carbon Nanodots: Emergent Nanolights", *Angewandte Chemie*, (2010), pp. 6726-6744, vol. 49, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, www.angewandte.org.

(Continued)

(21) Appl. No.: **14/627,404**

(22) Filed: **Feb. 20, 2015**

(65) **Prior Publication Data**

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Related U.S. Application Data

(62) Division of application No. 13/469,459, filed on May 11, 2012.

(60) Provisional application No. 61/486,090, filed on May 13, 2011.

(51) **Int. Cl.**

C09K 11/65 (2006.01)
C07C 215/08 (2006.01)
C09K 11/06 (2006.01)
B82Y 20/00 (2011.01)

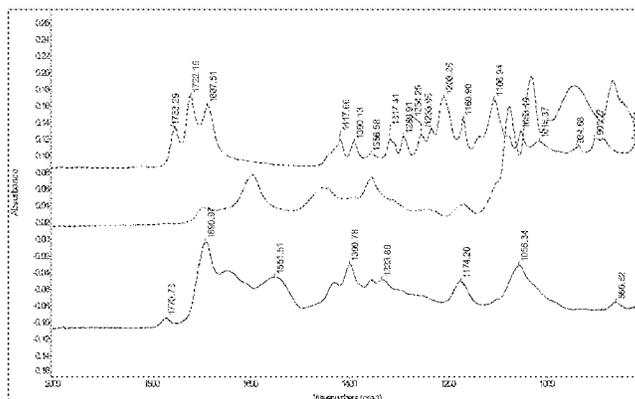
(52) **U.S. Cl.**

CPC **C09K 11/65** (2013.01); **C07C 215/08** (2013.01); **C09K 11/06** (2013.01); **B82Y 20/00**

(57) **ABSTRACT**

The present invention relates to carbon-based fluorescent nano-agent tracers for analysis of oil reservoirs. The carbon-based fluorescent nano-agents may be used in the analysis of the porosity of a formation. The nanoagents are suitable for injection into a petroleum reservoir and may be recovered from the reservoir for the determination of hydrocarbon flow rates and retention times.

14 Claims, 13 Drawing Sheets





US010047283B2

(12) **United States Patent**
Kanj et al.

(10) **Patent No.:** **US 10,047,283 B2**

(45) **Date of Patent:** ***Aug. 14, 2018**

(54) **CARBON-BASED FLUORESCENT TRACERS AS OIL RESERVOIR NANO-AGENTS**

(52) **U.S. Cl.**
CPC **C09K 11/06** (2013.01); **B82Y 20/00** (2013.01); **C01B 32/15** (2017.08); **C07C 215/08** (2013.01);

(71) Applicants: **Saudi Arabian Oil Company**, Dhahran (SA); **Cornell University**, Ithaca, NY (US)

(Continued)

(58) **Field of Classification Search**
None
See application file for complete search history.

(72) Inventors: **Mazen Y. Kanj**, Dhahran (SA); **Mohammad Harunar Rashid**, Ithaca, NY (US); **Emmanuel Giannelis**, Ithaca, NY (US)

(56) **References Cited**

(73) Assignees: **Saudi Arabian Oil Company**, Dhahran (SA); **Cornell University**, Ithaca, NY (US)

3,271,307 A 9/1966 Dickson et al.
3,292,696 A 12/1966 Sandiford
(Continued)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 8 days.

FOREIGN PATENT DOCUMENTS

This patent is subject to a terminal disclaimer.

WO 2007050984 A2 5/2007

(21) Appl. No.: **15/351,096**

OTHER PUBLICATIONS

(22) Filed: **Nov. 14, 2016**

Baker, S.N. and Baker, G.A., Luminescent Carbon Nanodots: Emergent Nanolights, Angewandte Chemie, (2010), pp. 6726-6744, vol. 49, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, www.angewandte.org.

(65) **Prior Publication Data**

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Primary Examiner — Jeffrey Washville
(74) *Attorney, Agent, or Firm* — Bracewell LLP; Constance G. Rhebergen; Brian H. Tompkins

Related U.S. Application Data

(57) **ABSTRACT**

(60) Continuation of application No. 14/627,404, filed on Feb. 20, 2015, now Pat. No. 9,528,045, which is a (Continued)

The present invention relates to carbon-based fluorescent nano-agent tracers for analysis of oil reservoirs. The carbon-based fluorescent nano-agents may be used in the analysis of the porosity of a formation. The nanoagents are suitable for injection into a petroleum reservoir and may be recovered from the reservoir for the determination of hydrocarbon flow rates and retention times.

(51) **Int. Cl.**
C09K 11/06 (2006.01)
C07H 15/04 (2006.01)

(Continued)

14 Claims, 13 Drawing Sheets

