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(54) **INERT FLUID ASSAYS FOR SEALED CORE RECOVERY**

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G01N 30/68 (2006.01)
G01N 9/00 (2006.01)
(Continued)

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CPC *G01N 30/68* (2013.01); *G01N 9/00* (2013.01); *G01N 33/2823* (2013.01); *G01N 2030/025* (2013.01)

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

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,986,555 A	10/1976	Roberstson
4,230,192 A	10/1980	Pfannkuche
	(Continued)		

FOREIGN PATENT DOCUMENTS

GB	2184835 A	7/1987
GB	2293653 A	4/1996
	(Continued)	

OTHER PUBLICATIONS

International Search Report and Written Opinion for application No. PCT/US22/40338 dates Dec. 19, 2022.

(Continued)

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(57) **ABSTRACT**

Methods of determining if a test fluid is inert to reservoir oil at RTP, by assaying a composition, density and bubble or dew point of live oil to generate a first dataset, equilibrating a sample of live oil with a test fluid at RTP to generate an oil phase; assaying a composition, density and bubble or dew point of the oil phase to generate a second dataset; comparing the first and second datasets, wherein significant changes in the datasets indicate that the test fluid is not inert to reservoir oil at RTP. By contrast, if there are no significant changes, the test fluid is inert, and would therefore be suitable to collecting core samples at RTP. Various options for inert fluids are also provided.

17 Claims, 13 Drawing Sheets

CONSTANT COMPOSITION EXPANSION @ 303.0F
RELATIVE VOLUME AS A FUNCTION OF PRESSURE
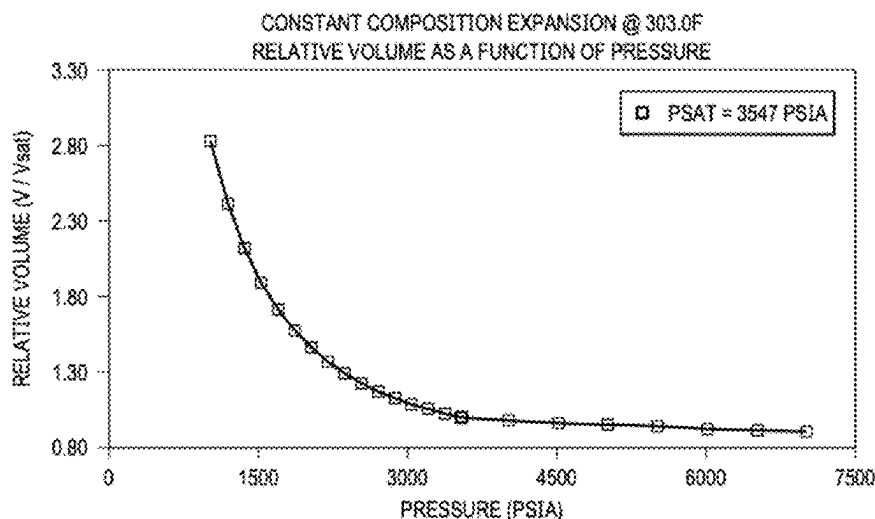
(51) **Int. Cl.**
    G01N 30/02   (2006.01)
    G01N 33/28   (2006.01)

(56)   **References Cited**

U.S. PATENT DOCUMENTS

4,256,192	A	3/1981	Aumann
4,258,803	A	3/1981	Thompson et al.
4,573,342	A	3/1986	Jones
4,649,737	A	3/1987	Jones
4,702,168	A	10/1987	Colle et al.
4,950,844	A	8/1990	Hallmark
5,193,059	A	3/1993	Tiab et al.
5,263,360	A	11/1993	Blauch et al.
5,265,462	A	11/1993	Blauch et al.
5,297,420	A	3/1994	Gilliland et al.
5,359,194	A	10/1994	Moss
5,741,959	A	4/1998	Garcia et al.
6,642,056	B1 *	11/2003	Correra G01N 33/2823
			436/139
7,347,284	B2	3/2008	Arian et al.
7,600,580	B2	12/2009	Caravatte et al.
8,122,976	B2	2/2012	Bartelle et al.
8,256,282	B2	9/2012	Schlachter
8,230,946	B2	11/2012	Crawford et al.
8,307,704	B2	11/2012	Georgi et al.
8,356,510	B2	1/2013	Coenen
8,453,766	B2	6/2013	Graterol et al.
8,621,920	B2	1/2014	Reid et al.
9,051,804	B2	6/2015	Reid et al.
9,243,466	B2	1/2016	Klomp
9,291,541	B2	3/2016	Kim et al.
9,376,879	B2	6/2016	Mizuguchi
9,506,307	B2	11/2016	Kinsella
9,745,811	B2	8/2017	Wesemeier et al.
9,828,820	B2	11/2017	Gupta et al.
9,874,063	B2	1/2018	Arian et al.
9,926,756	B2	3/2018	Wesemeier et al.
9,951,574	B2	4/2018	Westacott et al.
10,047,580	B2	8/2018	Morgan et al.
10,174,613	B2	1/2019	Quintero et al.
10,221,684	B2	3/2019	Westacott et al.
10,260,300	B2	4/2019	Dorovsky et al.
10,301,936	B2	5/2019	Westacott et al.
10,317,351	B2	6/2019	Chong et al.
10,550,655	B2	2/2020	Jones et al.
10,761,157	B2	9/2020	Chen et al.
2010/0126266	A1	5/2010	Coenen

2013/0197809	A1 *	8/2013	Jones G01N 1/00
			73/864.91
2014/0090835	A1	4/2014	Griffin
2014/0130581	A1 *	5/2014	Ovalles C09K 8/04
			208/309
2014/0208826	A1 *	7/2014	Larter G01N 11/00
			356/70
2015/0354352	A1	12/2015	Ezzat et al.
2017/0089158	A1 *	3/2017	Gupta G01N 33/24
2018/0148988	A1	5/2018	Dusterhoft et al.
2018/0298709	A1 *	10/2018	Gupta G01V 5/04
2018/0371904	A1	12/2018	Zuilekom et al.

FOREIGN PATENT DOCUMENTS

WO	2019070252 A1	4/2019
WO	2019090316 A1	5/2019

OTHER PUBLICATIONS

Kenyon, W.E. Petrophysical Principles of Applications of NMR Logging. The Log Analyst (2009) 38 (2): 21-43.

Murphy, D.P. 1995. NMR logging and core analysis—simplified. World Oil (1995) 216 (4): 65-70. OSTI ID 39931.

Woessner, D.E. The early days of NMR in the Southwest. Concepts in Magnetic Resonance (2001)13 (2): 77-102.

Zhao, T.; Verma S.; Devegowda, D.; Jayaram, V. TOC Estimation in the Barnett Shale From Triple Combo Logs Using Support Vector Machine. SEG Annual Meeting, 2015, Paper # SEG-2015-5922788.

Truax J.; Galford, J.; Moake, G.; Torres, D.; Cherry, R.; Mandal, B.; Mishra, A.; Martin, S. L.; Quintero, A. Performance of a new 2.35-in. wireline or memory quad combo for through-bit or small-hole logging. SPE Annual Technical Conference and Exhibition. 2011, Paper # SPE-147400-MS.

Clark, A. J. (2009). Determination of recovery factor in the Bakken formation, Mountrail County, ND. SPE Annual Technical Conference and Exhibition. 2009, Paper # SPE-133719-STU.

Alhashim, H. W.; Zhang, F.; Schechter, D. S.; Chen J-H. Investigation of the effect of pore size distribution on the produced oil from surfactant-assisted spontaneous imbibition in ULRs. SPE Annual Technical Conference and Exhibition. SPE-195931-MS.

Dunn, K.-J.; Bergman, D.J.; Latorraca, G.A. Nuclear Magnetic Resonance Petrophysical and Logging Applications. (2002) vol. 32, New York: Handbook of Geophysical Exploration: Seismic Exploration, Pergamon Press.
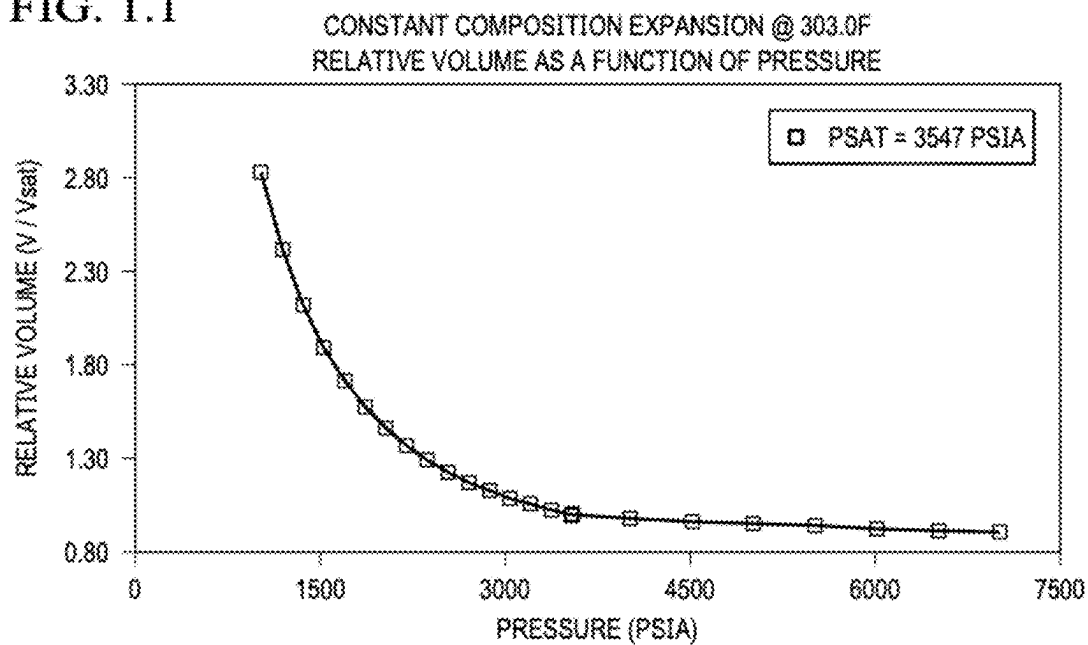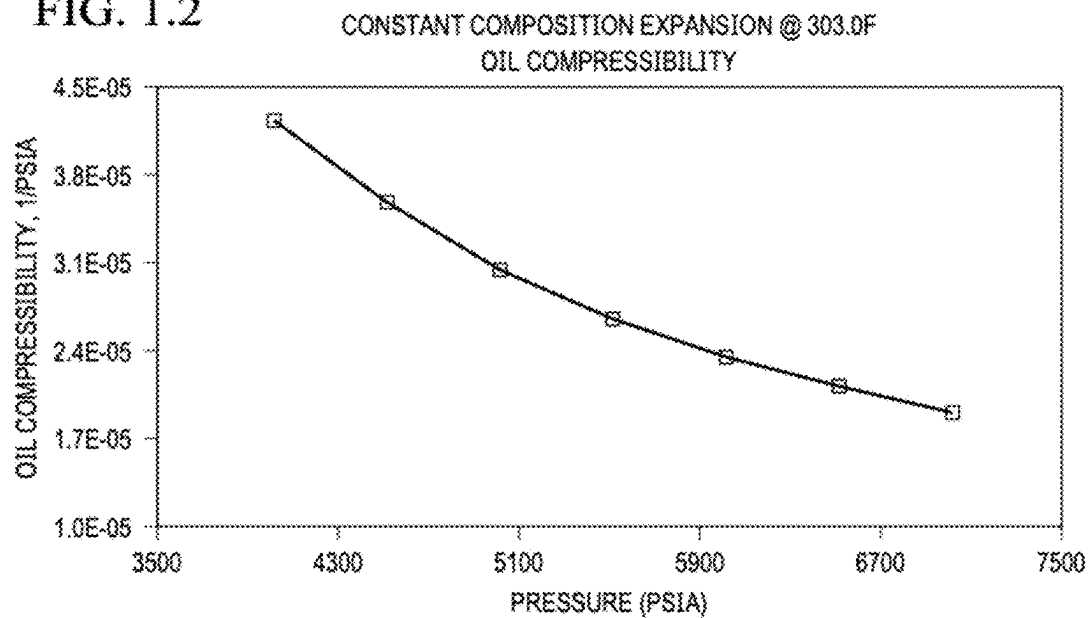
* cited by examiner

FIG. 1.1

CONSTANT COMPOSITION EXPANSION @ 303.0F
RELATIVE VOLUME AS A FUNCTION OF PRESSURE

FIG. 1.2

CONSTANT COMPOSITION EXPANSION @ 303.0F
OIL COMPRESSIBILITY

FIG. 2.1

CONSTANT COMPOSITION EXPANSION OF LIVE OIL / FC-40 FLUID SYSTEM @ 303.0F
RELATIVE VOLUME AS A FUNCTION OF PRESSURE

FIG. 2.2

CONSTANT COMPOSITION EXPANSION OF LIVE OIL / FC-40 FLUID SYSTEM @ 303.0F
LIVE OIL / FC-40 FLUID SYSTEM
COMPRESSIBILITY AS A FUNCTION OF PRESSURE
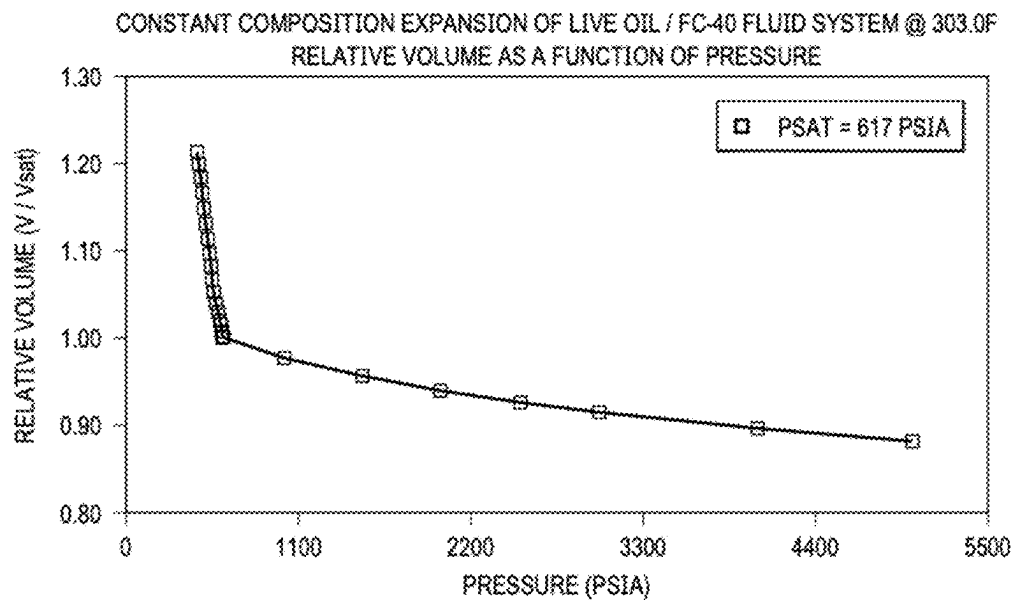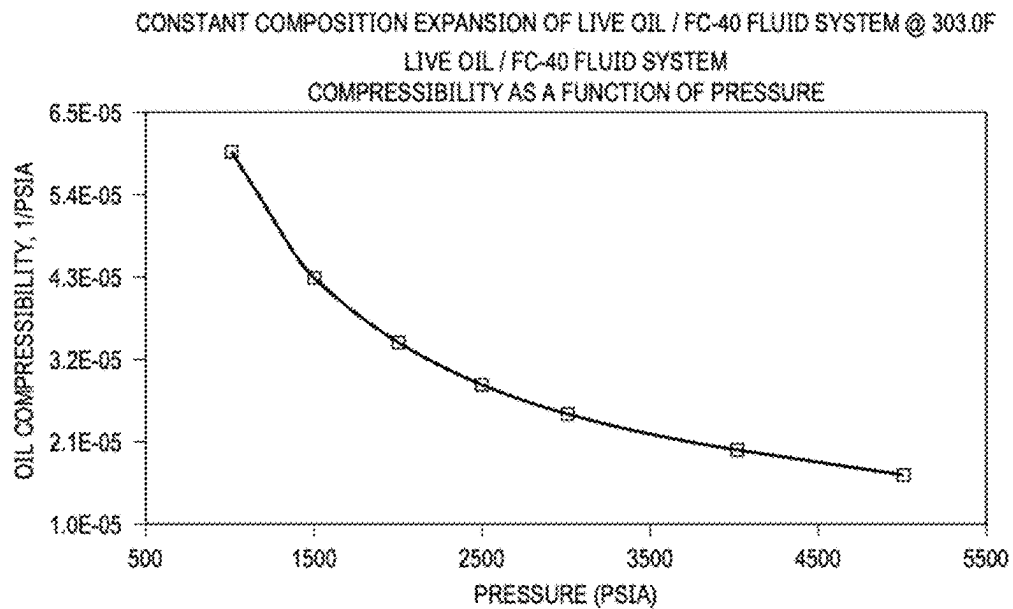
CONSTANT COMPOSITION EXPANSION PICTURES
OIL BEFORE CONTACT WITH FC-40

OIL

PRESSURE 4999.3 Psi
VOLUME 59.572 cc
TEMPERATURE 303.0 °F

CELL PISTON

FIG. 3

INITIAL CONTACT WITH FC-40

PRESSURE 4998.4 Psi
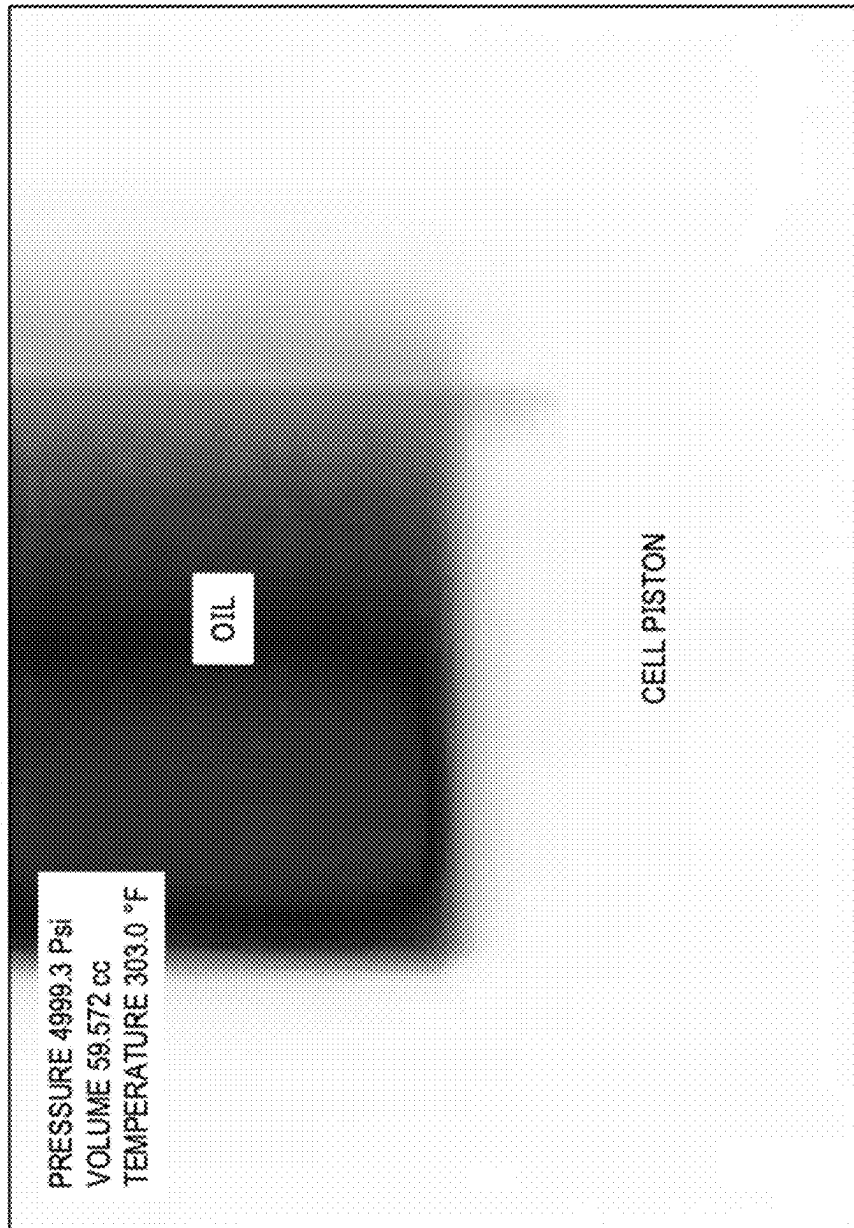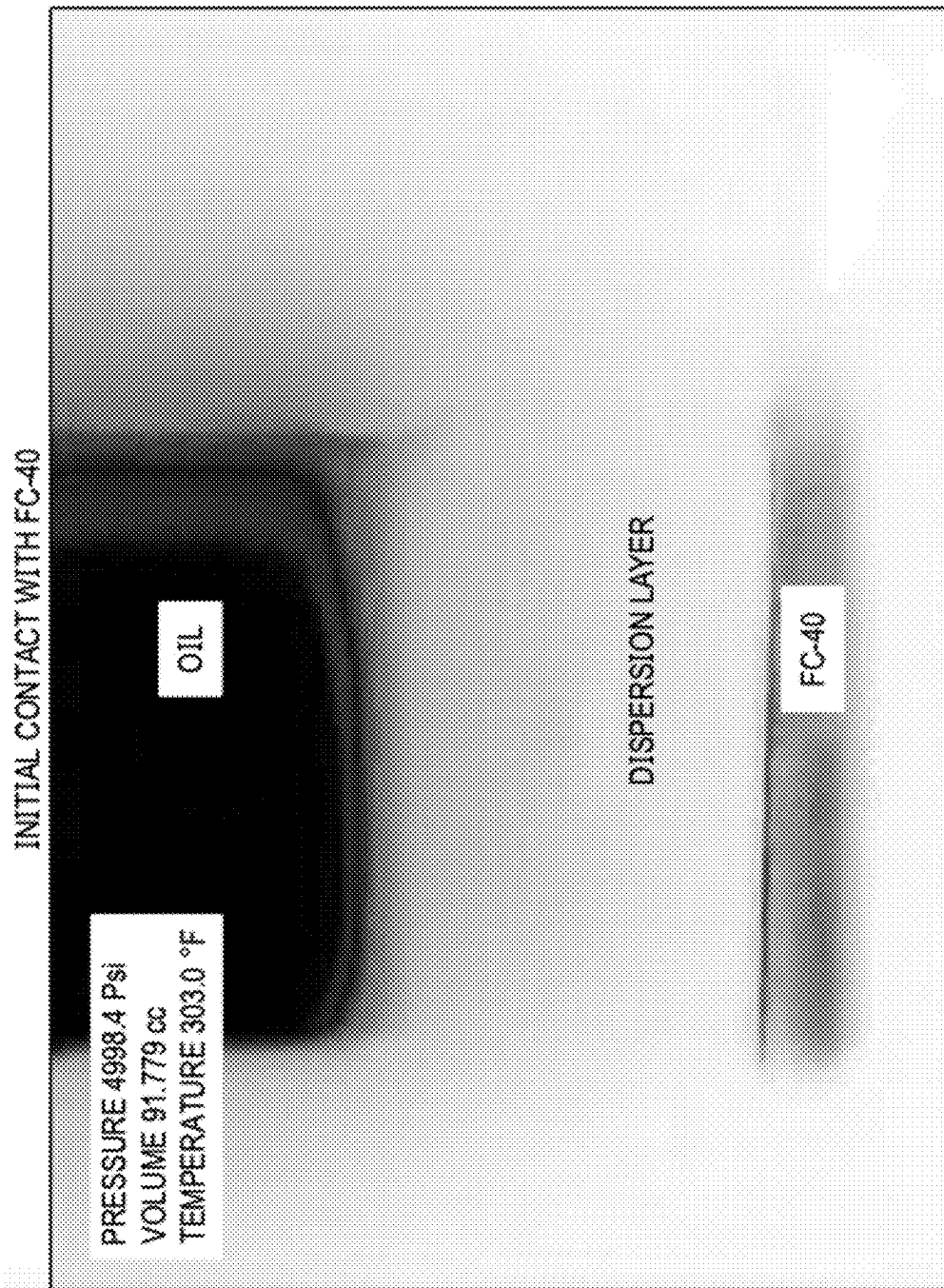VOLUME 91.779 cc
TEMPERATURE 303.0 °F

OIL

DISPERSION LAYER

FC-40

FIG. 4

CONSTANT COMPOSITION EXPANSION PICTURES
OIL / FC-40 INITIAL INTERFACE (NO MIXING)

OIL

DISPERSION LAYER

FC-40

PRESSURE 4998.4 Psi
VOLUME 103.495 cc
TEMPERATURE 303.0 °F

FIG. 5

OIL / FC-40 DISPERSION LAYER (NO MECHANICAL MIXING)

PRESSURE 5002.0 Psi
VOLUME 305.446 cc
TEMPERATURE 302.3 °F

OIL

DISPERSION LAYER

FC-40
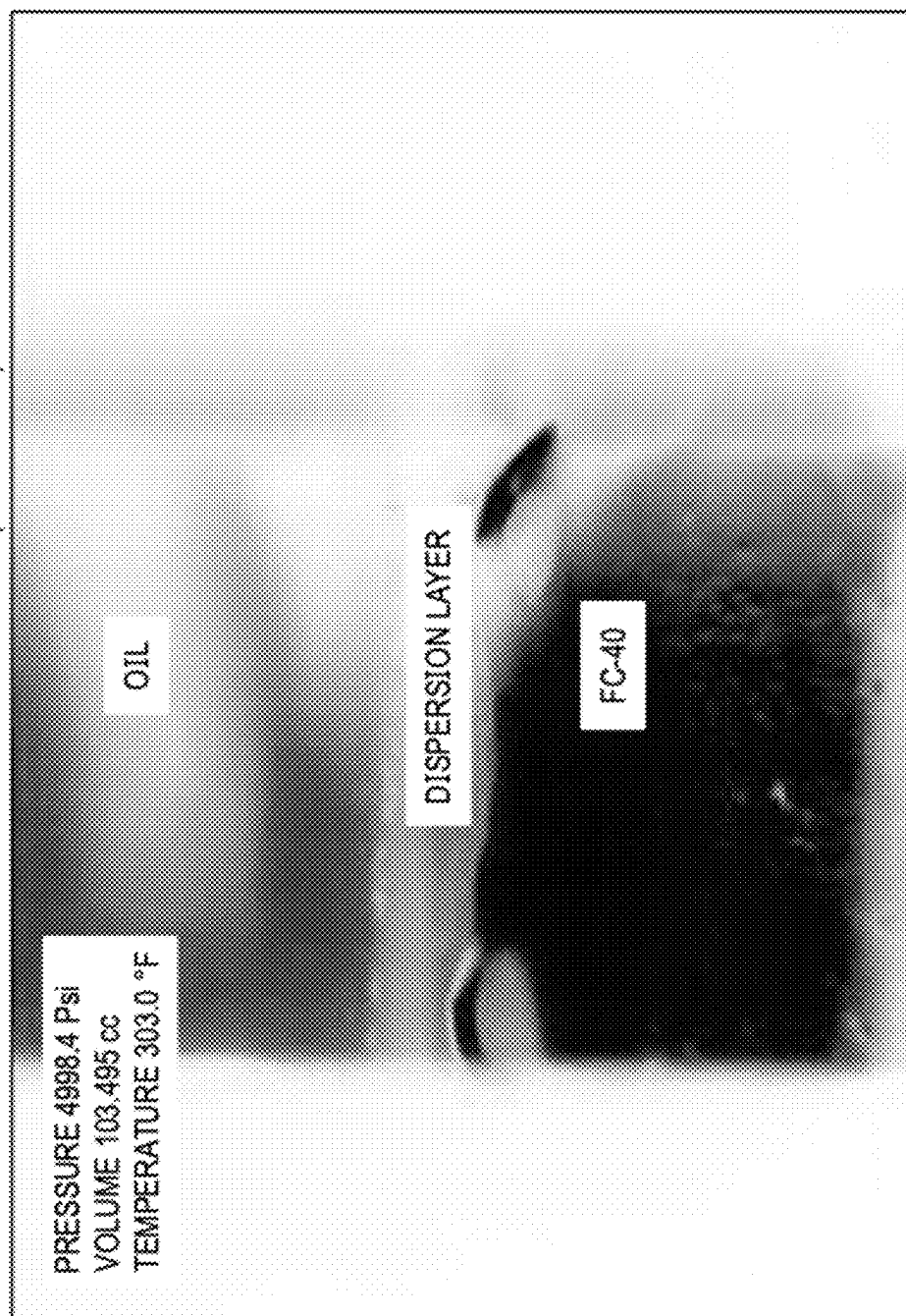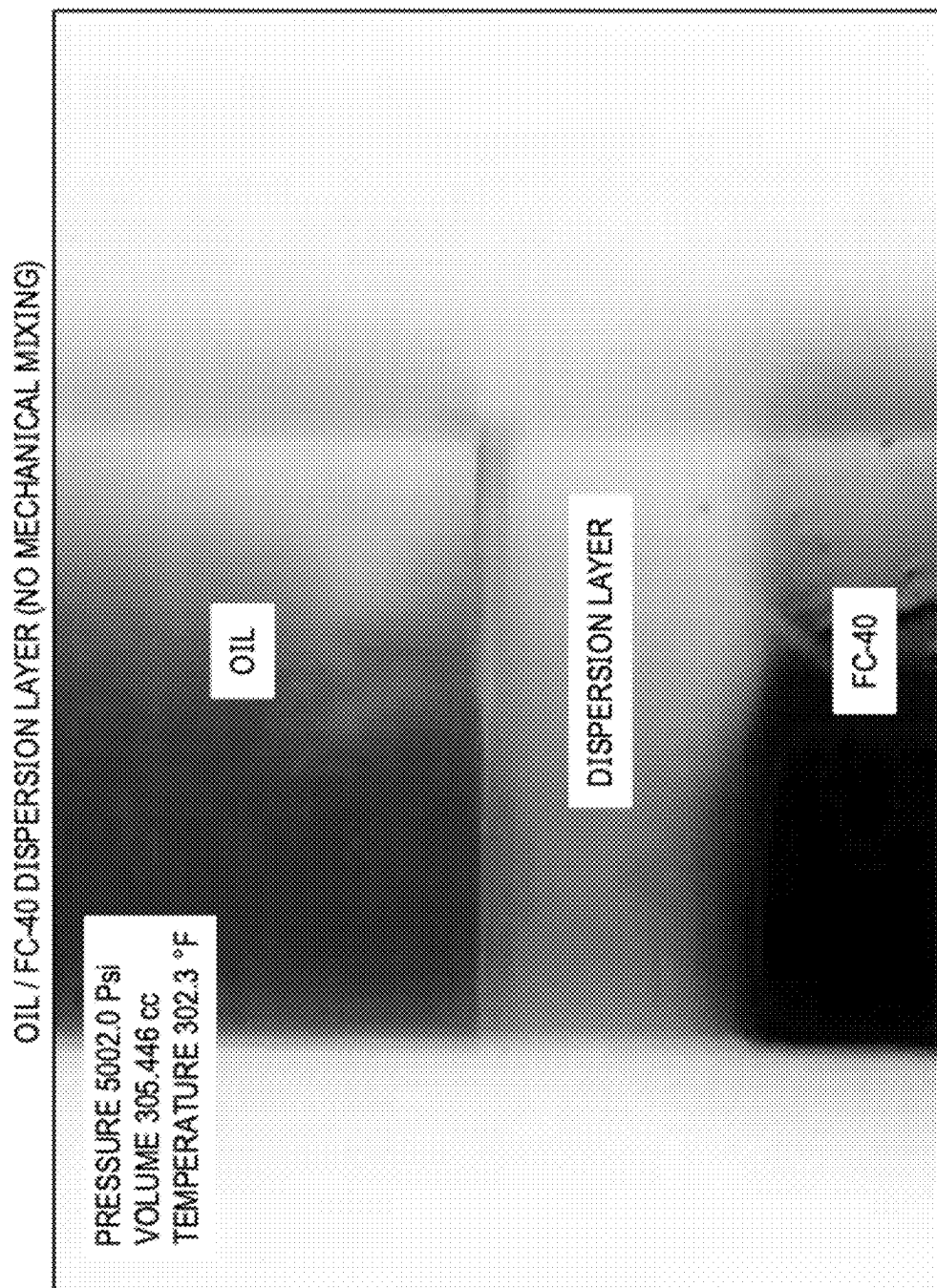
FIG. 6

CONSTANT COMPOSITION EXPANSION PICTURES
OIL / FC-40 DISPERSION LAYER 2 (NO MECHANICAL MIXING)

PRESSURE 5002.0 Psi
VOLUME 327.133 cc
TEMPERATURE 302.1 °F

OIL

DISPERSION LAYER

FC-40

FIG. 7

FIG. 8

CONSTANT COMPOSITION EXPANSION PICTURES

OIL / FC-40 INTERFACE FLUID CHANGE DURING MECHANICAL MIXING

OIL

FC-40

PRESSURE 5000.2 Psi
VOLUME 373.823 cc
TEMPERATURE 304.1 °F
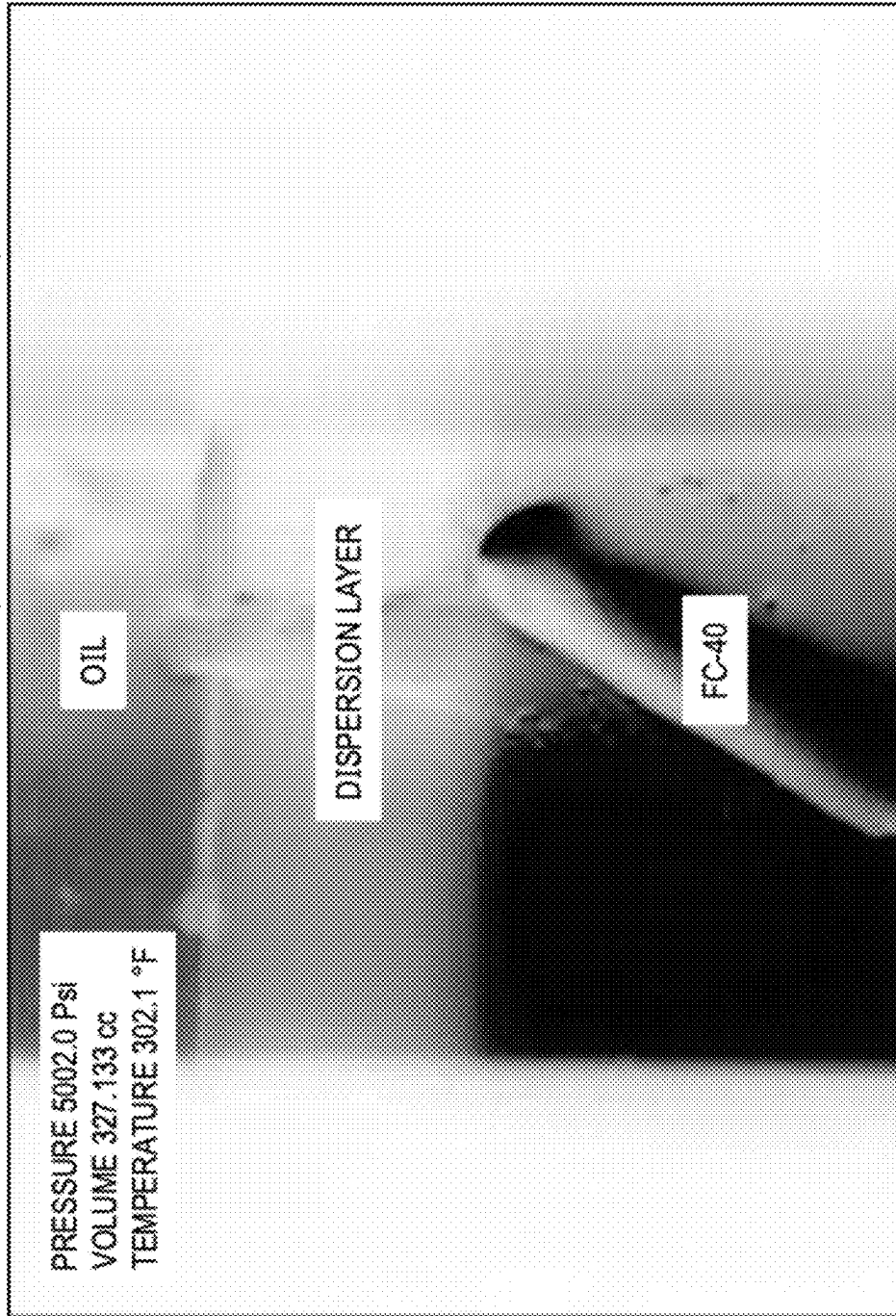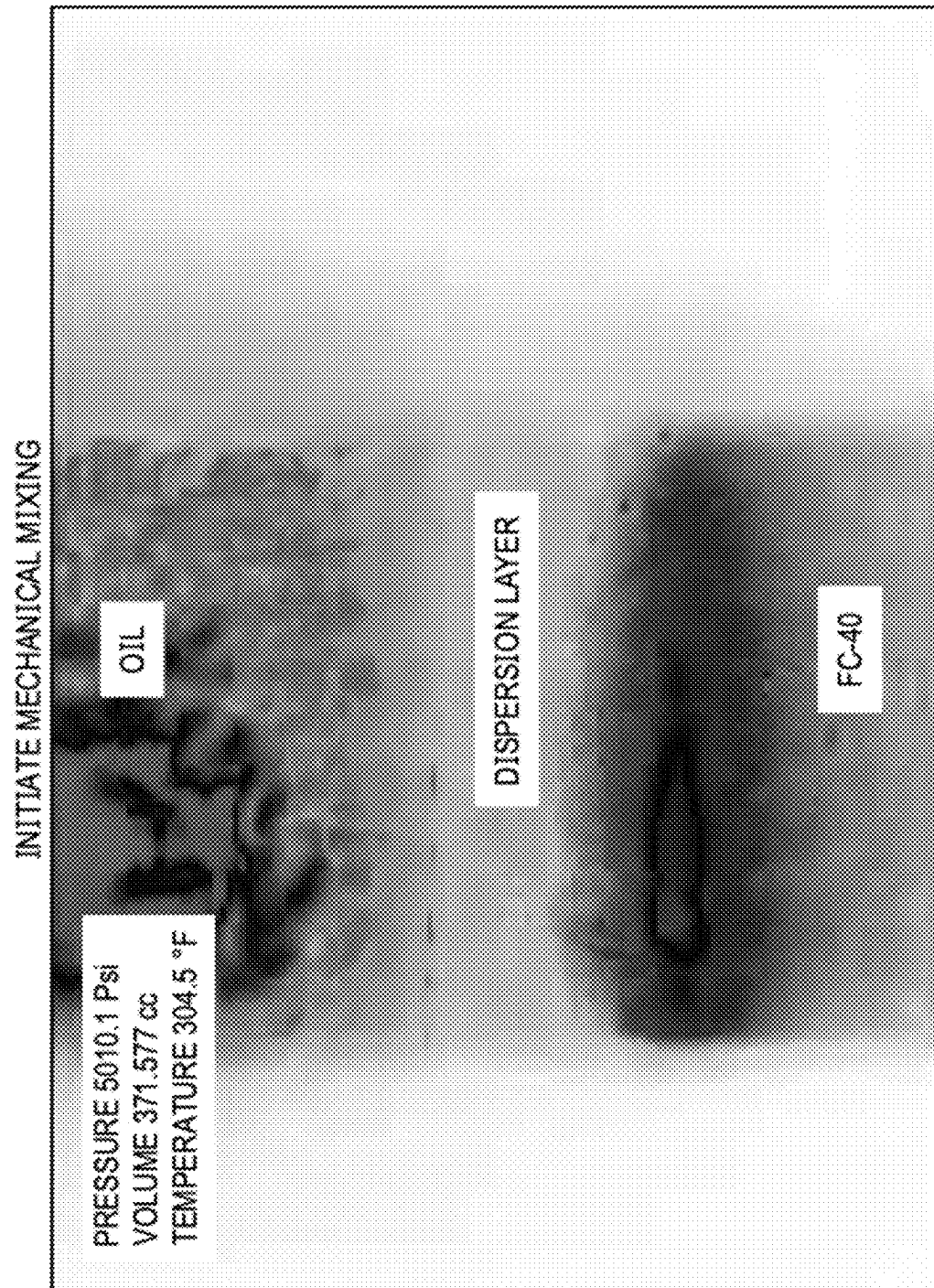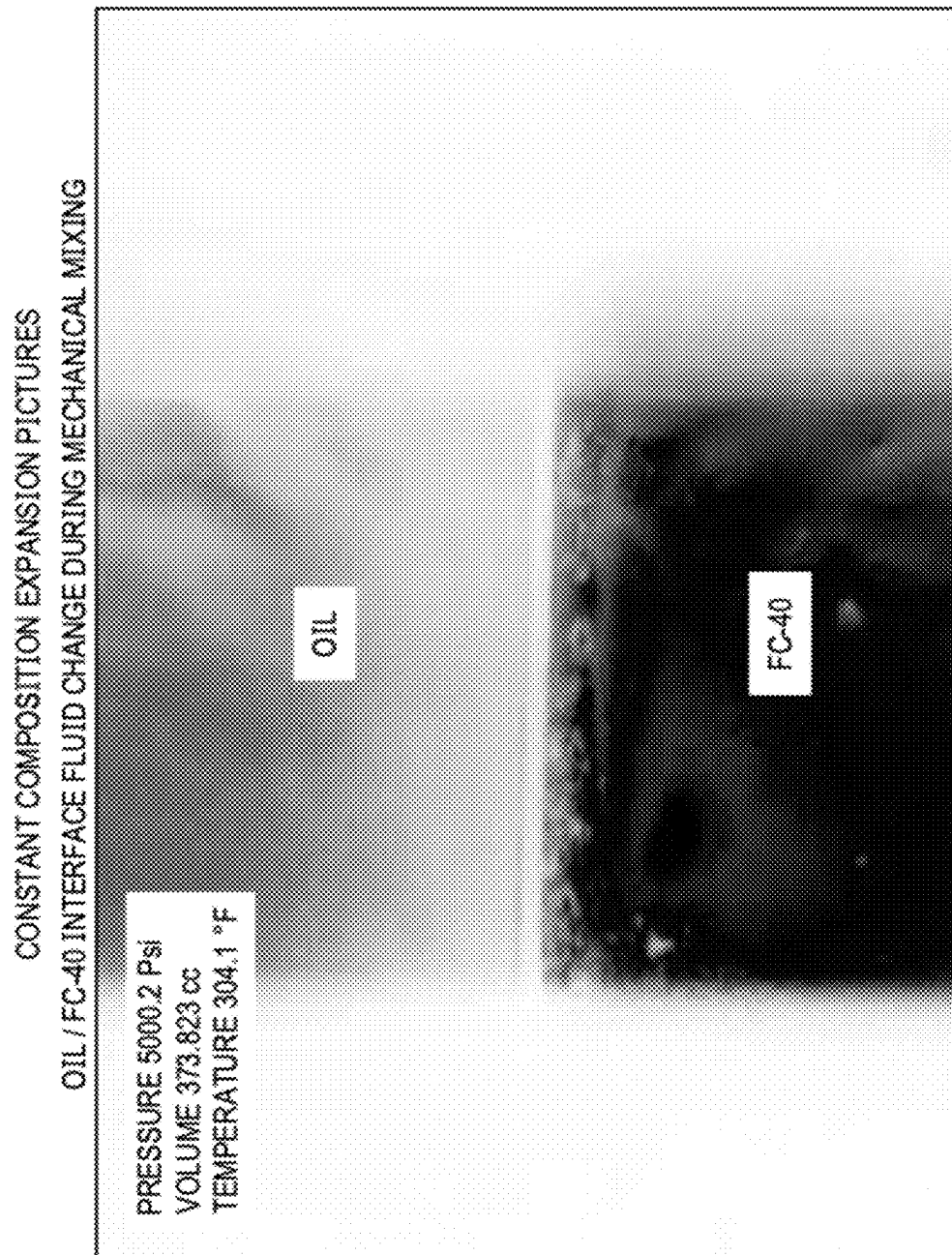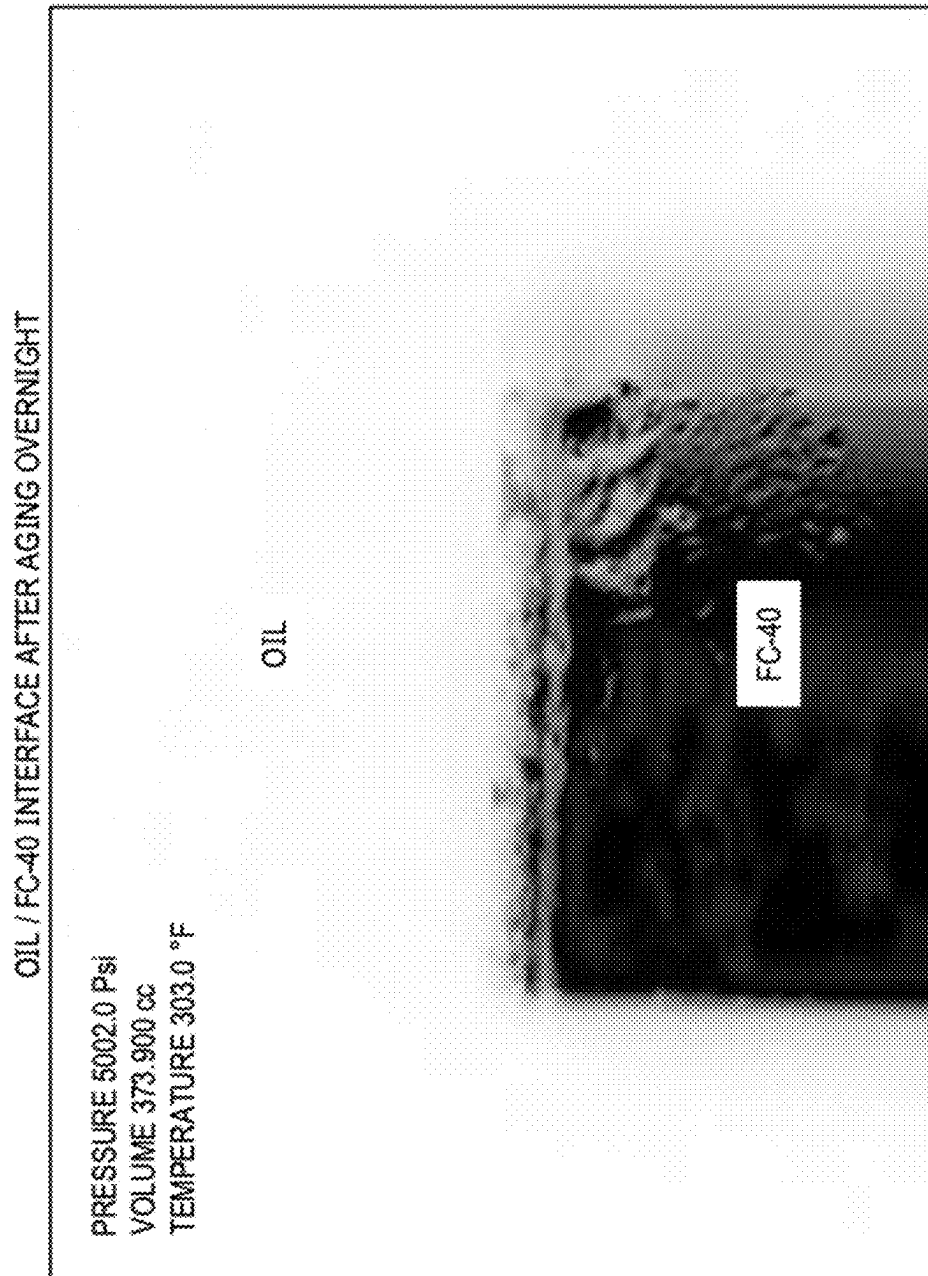
FIG. 9

FIG. 10

CONSTANT COMPOSITION EXPANSION PICTURES
OIL / FC-40 INTERFACE AT SATURATION PRESSURE

PRESSURE 605.2 Psi
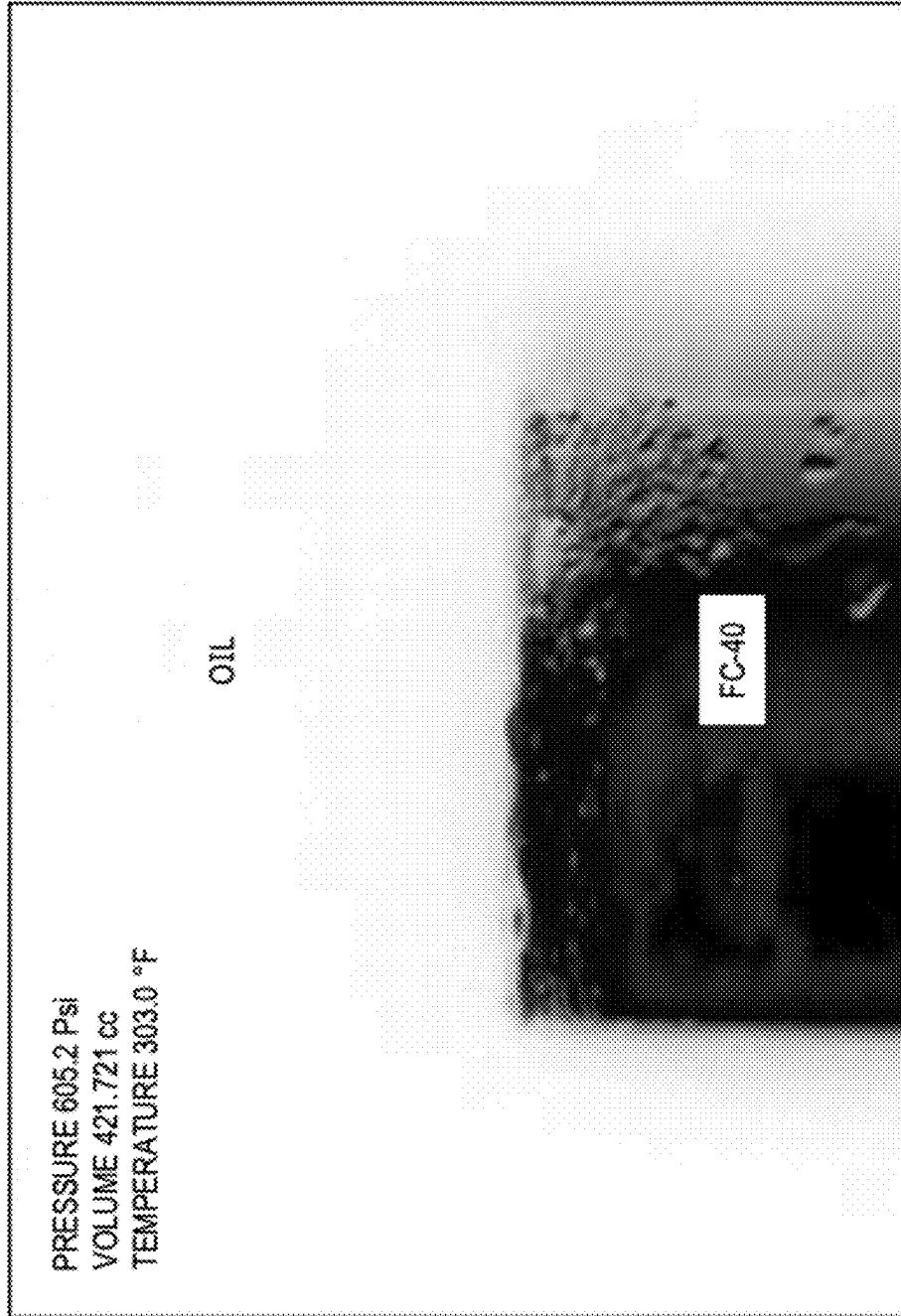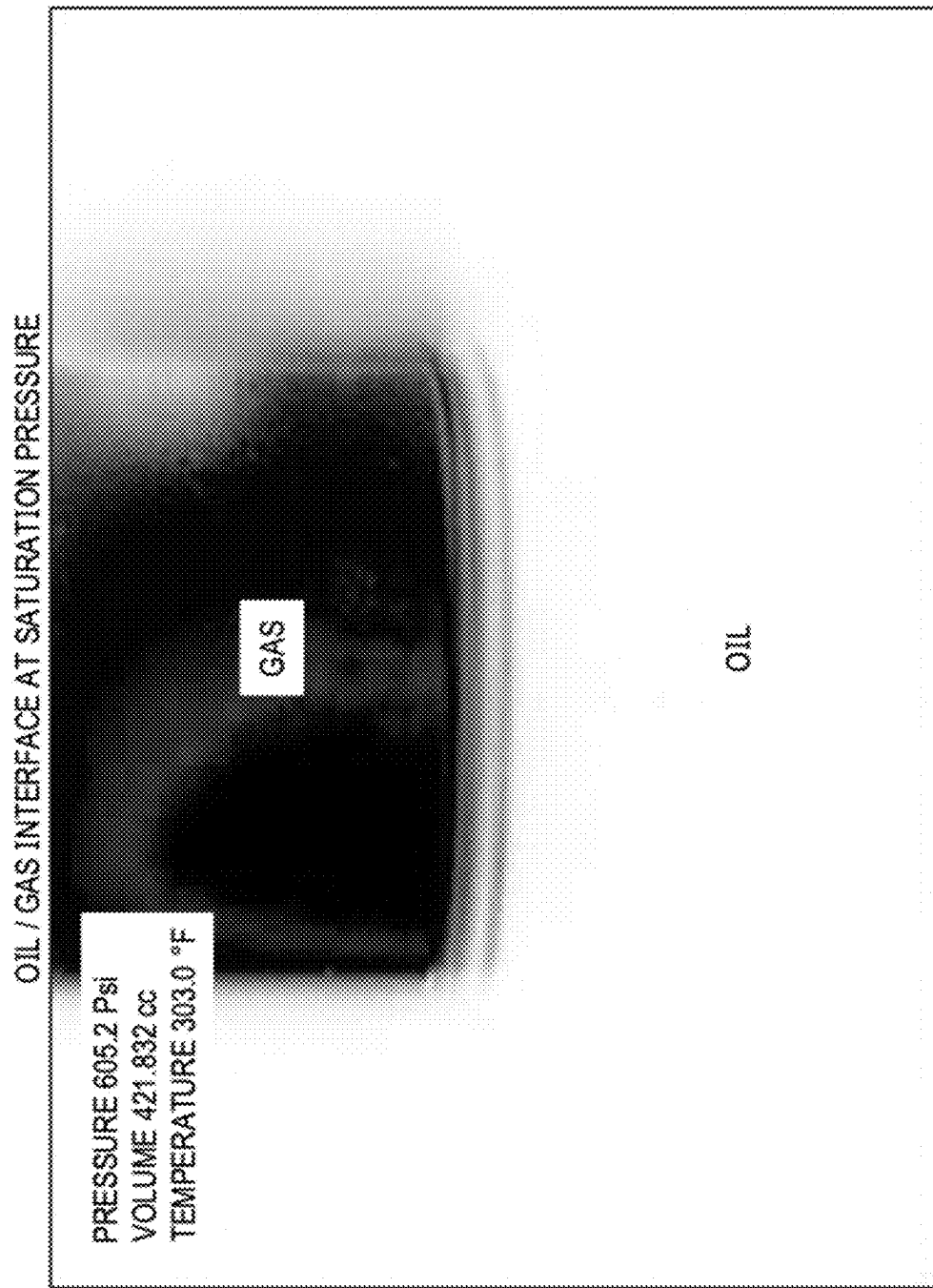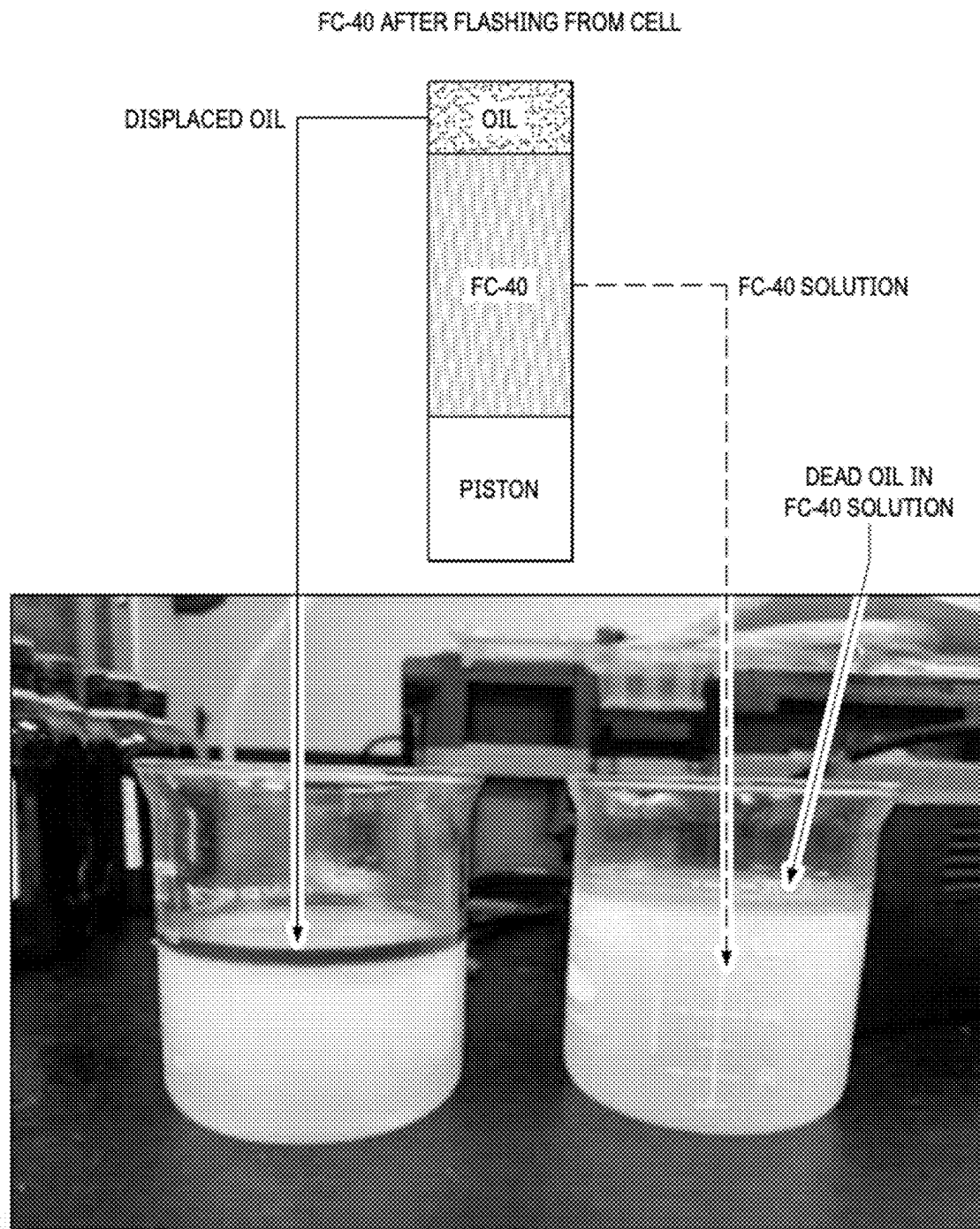VOLUME 421.721 cc
TEMPERATURE 303.0 °F

OIL

FC-40

FIG. 11

OIL / GAS INTERFACE AT SATURATION PRESSURE

PRESSURE 605.2 Psi
VOLUME 421.832 cc
TEMPERATURE 303.0 °F

GAS

OIL

FIG. 12

FIG. 13

INERT FLUID ASSAYS FOR SEALED CORE RECOVERY

PRIOR RELATED APPLICATIONS

This application claims priority to U.S. Ser. No. 63/244,953, filed Sep. 16, 2021, and incorporated by reference in its entirety for all purposes.

FIELD OF THE DISCLOSURE

This disclosure provides methods of testing core preservation fluids for drilling core samples and returning them to the surface in an unchanged condition.

BACKGROUND OF THE DISCLOSURE

One of the ways of studying rock characteristics is to drill and analyze a core sample from a reservoir. Similar to a drill bit, the rotary coring bit consists of solid metal with diamonds or tungsten for cutting at the reservoir rock, but unlike a drill bit, a rotary coring bit has a hollow center. The cutting apparatus thus surrounds the hollow center, called the core barrel, where the core sample is stored. The core barrel is made up of an inner and outer barrel separated by ball bearings, which allows the inner barrel to remain stationary and retain the core sample, while the outer barrel is rotated by the drill string and cuts the core. The core catcher is located within the core barrel and has finger-like apparatuses that move the core sample farther into the barrel and keep it from falling back into the well. After the core sample has been cut from the well, the drill string is raised, and the rotary coring bit, barrel and catcher are removed, and the core sample is retrieved. The drill bit is reattached, and drilling can commence again.

However, obtaining an unaltered core sample from a reservoir with these simple prior art devices remains challenging. As the core is retrieved from deep in the reservoir, the temperature and pressure decrease which allows gases to evolve out of solution and together with free gases, expand, resulting in reservoir fluids being forced out of the core. Thus, accurate sampling, especially of fluids, is difficult, if not impossible to obtain.

To address this problem, the core samples are sometimes collected and sealed in a chamber, in a method known as "pressure coring". Pressure coring at least partially solves the problem by maintaining the core specimen at bottom-hole pressure—BHP—until the core fluids can be recovered. This concept, first proposed by Sewell in the 1930's, remained a "laboratory" tool until the late 1970's, but with the advent of ever improving technology, the method is much more popular now.

However, in pressure coring the core samples are contained in an inert fluid known as FC-40 aka FLUORINERT™ which was developed for electronic uses, not uses in the petroleum industry. FC-40 is a colorless, thermally stable, fully fluorinated liquid that was believed to be inert, even at reservoir temperature and pressure (RTP). With the data presented herein, we now know that it in fact solubilizes

some of the lighter fractions of oil, and thus skewing the results of high pressure core analysis. The discrepancy arises from the fact that standard testing techniques are wholly inappropriate for use with a so-called "inert" fluid developed for electronic uses, as opposed to downhole uses.

This disclosure for the first time provides assays and methodology to correctly assay downhole core samples, and further develop novel inert, high density fluids for use in obtaining and analyzing reservoir core samples.

SUMMARY OF THE DISCLOSURE

FC-40 contains C_{5-18} perfluorocarbon chains, that are largely inert to electronics, but less so for petroleum, which contains short, medium, and long chain hydrocarbons. Table A provides the known FC-40 properties:

TABLE A

FC-40	
1. Information on basic physical and chemical properties	
General Physical Form:	Liquid
Specific Physical Form:	Liquid
Odor, Color, Grade:	Colorless, odorless liquid.
Odor threshold	No Data Available
pH	Not Applicable
Melting point	Not Applicable
Boiling Point	158-173° C.
Flash Point	No flash point
Evaporation rate	<1 [RefStd:BUOAC = 1]
Flammability (solid, gas)	Not Applicable
Flammable Limits(LEL)	None detected
Flammable Limits(UEL)	None detected
Vapor Pressure	3 mmHg [@ 25° C.]
Vapor Density	22.5 [@ 25° C.] [Ref St: AIR = 1]
Density	1.9 g/ml
Specific Gravity	1.9 [RefStd:WATER = 1]
Solubility in Water	Nil
Solubility—non-water	No Data Available
Partition coefficient: n-octanol water	No Data Available
Autoignition temperature	No Data Available
Decomposition temperature	No Data Available
Viscosity	2 centistoke [@ 25° C.]
Molecular weight	No Data Available
Volatile Organic Compounds	[Details: Exempt]
Percent volatile	100%
VOC Less H2O & Exempt Solvents	[Details: Exempt]

As is apparent, FC-40 is not particularly viscous, but is fairly dense at 1.9 g/ml. Insomuch as electronics are concerned, it is fairly inert, but as demonstrated herein, light hydrocarbons have significant solubility in FC-40, even at atmospheric conditions, and at reservoir temperature and pressure (RTP), the problem is greatly exacerbated.

Thus, what is needed in the art are test methods for correctly assaying inert fluids for downhole uses. Such assays would allow the art to develop new materials that do not dissolve light hydrocarbons but is otherwise as dense and inert to the full range of petroleum constituents, especially at RTP. In the absence of an absolute inert fluid, characterization of solubility in FC-40 and other fluids at atmospheric and at reservoir conditions will provide methods to characterize interactions within the reservoir and simulate processes under reservoir conditions.

The invention includes any one or more of the following embodiments, any one or more of which can be combined with any other one or more in any combination(s) thereof.

A method of assaying a test fluid for collecting reservoir core samples at reservoir temperature and pressure (RTP) and determining if said test fluid is inert at RTP, said method comprising:
a) assaying live oil to generate a first dataset using methods comprising two or more of:

i) determining a weight contribution of components of said live oil;

ii) determining a bubble point of said live oil;

iii) determining a density of a remaining oil when saidlive oil is flashed to ambient conditions; or

iv) determining a weight contribution of gaseous components flashed from said live oil;

b) assaying live oil plus a test fluid mixed together and equilibrated at RTP to form a hydrocarbon phase and a test fluid phase to generate a second dataset, using methods comprising two or more of:

i) determining a bubble point of said hydrocarbon phase;

ii) determining a weight contribution of components of said hydrocarbon phase;

iii) determining a density of a remaining hydrocarbon phase when said hydrocarbon phase is flashed to standard temperature and pressure (STP) or ambient conditions; or

iv) determining a weight contribution of gaseous components flashed from said hydrocarbon phase;

c) comparing said first dataset and said second dataset, wherein changes in said datasets after equilibration with said test fluid indicates that said test fluid is not inert, but no changes in said datasets indicates said test fluid is inert and can be used to collect reservoir core samples at RTP.

Any method described herein could also use instead of i-iv) or in addition thereto, any one or more of the following: determining total acid number (TAN), metal content, viscosity, asphaltene content, C7 content; nitrogen content, water content, carbon content, total contents; wax content; carbon residue content, conductivity, pour point, density@15° C.; salt content, sediment content, specific gravity; light end hydrocarbon content; mercaptan content; hydrogen content, total sulfur, hydrogen sulfide content or vapor pressure of said hydrocarbon phase or said remaining hydrocarbon phase.

A method of assaying a test fluid for inertness in collecting reservoir core samples at RTP, said method comprising:

a) obtaining an oil sample having a first characterization of elements, C1-C40 components, dissolved gas and density;

b) mixing said oil sample plus a test fluid to form a mixture, and equilibrating said mixture at RTP to produce a hydrocarbon phase and a test fluid phase;

c) assaying said hydrocarbon phase to determine a second characterization of elements, C1-C40 components, dissolved gas and density;

d)comparing said first characterization with said second characterization to identify changes in characterization;

e) wherein changes in characterization indicates that said test fluid is not inert, but no changes in characterization indicates said test fluid is inert and can be used to collect reservoir core samples at RTP.

A method of determining if a test fluid is inert to reservoir oil at RTP, comprising:

a) assaying a composition, density and bubble or dew point of live oil to generate a first dataset;

b) equilibrating a sample of said live oil with a test fluid at RTP to generate a hydrocarbon phase;

c) assaying a composition, density and bubble or dew point of said hydrocarbon phase to generate a second dataset;

d) comparing said first and second datasets, wherein significant changes in said dataset indicates that said test fluid is not inert to reservoir oil at RTP.

Any method herein described, wherein weight contribution is determined with gas chromatography, preferably with GC/FID, but other methods could be used including HPLC, elemental analysis, and the like.

Any method herein described, wherein density of a fluid is determined using a HPHT densitometer at RTP.

Any method herein described, wherein bubble point of a fluid is determined by stepping down the pressure from RTP and observing a pressure at which bubbles appear or by ASTM D2889-95 (2019).

Any method herein described, wherein RTP is an average temperature and pressure of a play in the reservoir.

Although we focus on composition, density, and bubble or dew points herein, other characterization methods could also be used, e.g., measuring Acidity TAN—total acid number; metals; viscosity; asphaltene, C7; nitrogen basic; water content; carbon content; nitrogen, total content; wax content; carbon residue; phosphorous content; conductivity; pour point; density@15° C.; salt; distillation; sediments, gravity; silicon content; light end hydrocarbons; sulfur, mercaptans; hydrogen content; sulfur, total; hydrogen sulfide; vapor pressure and the like. These can be added to the characterization sets or in many cases substituted therefor. For example, in our experiments it would have sufficed to test for light ends only.

As used herein, "brominated" or "fluorinated" means to replace one or more hydrogens with bromine or fluorine.

As used herein, "perbrominated" or "perfluorinated" is to combine with the maximum amount of fluorine especially in place of hydrogen.

As used herein, "high pressure" means higher than 1 atm, and includes all typical downhole pressures (e.g. up to and even beyond 25,000 psi).

As used herein, a "high temperature" means reservoir temperatures which are greater than 100° F., typically about 200-400° F. in a reservoir.

As used herein "live oil" is oil containing dissolved gas in solution that may be released from the oil solution at surface conditions. Live oil must be handled and pumped under closely controlled conditions to minimize the risk of explosion or fire.

As used herein "dead oil" is oil that has been flashed to STP or ambient conditions at the surface and no longer containing very much dissolved gas.

As used herein, "bubble point" or "bubble-point pressure" is defined as the temperature and pressure at which gas begins to break out of an under saturated oil and form a free gas phase in the matrix or a gas cap. In layman's terms it may be thought of as the pressure at which the first bubble of gas appears at a specific temperature. The phase diagram of typical black oils shows that the bubble-point pressure could be different at different temperatures and pressures dependent upon many factors including gas concentration and oil composition. Often the oil is saturated with gas when discovered, meaning that the oil is holding all the gas it can at the reservoir temperature and pressure, and that it is at its bubble point. Occasionally, the oil will be undersaturated. In this case, as the pressure is lowered, the pressure at which the first gas begins to evolve from the oil is defined as the bubble point. In the petroleum industry, if bubble-point pressure value is mentioned without reference to a particular temperature, the temperature is implicitly assumed to be the reservoir temperature.

As used herein, "reservoir T" or "reservoir P" or "reservoir TP" or "RTP" refer to reservoir temperature, reservoir pressure, or reservoir temperature and pressure conditions at the depth the hydrocarbon is found at. If the depth of the play is significant, an average RTP within the play can be used.

As used herein, "standard TP" or "STP" is defined as a temperature of 273.15 K (0° C., 32° F.) and an absolute pressure of exactly 105 Pa (100 kPa, 1 bar). Standard temperature and pressure in the oil industry may vary, however, as standard temperature is 15° C. and pressure may vary by state regulations. Further, many use ambient conditions in the lab instead as providing for easier experiments.

As used herein, "saturation pressure" is the pressure at a given temperature where the fluid goes into the two-phase region (from a one-phase region). The two-phase region may be influenced by gas concentration and oil composition at a given reservoir temperature and pressure. The vapor pressure of a liquid can be defined as the saturation pressure at ambient temperature. Inversely, the saturation pressure of a gas condensate is its dewpoint pressure. Saturation pressure is equivalent to bubble point pressure at a given pressure and temperature below the critical point. At temperatures above the critical point, the saturation pressure is equivalent to dew point until a single phase gas reservoir is reached at an upper temperature.

As used herein, "zero-flash" refers to flashing a live oil sample to standard conditions in a closed loop system so that nothing escapes.

The use of the word "a" or "an" in the claims or the specification means one or more than one, unless the context dictates otherwise.

The term "about" means the stated value plus or minus the margin of error of measurement or plus or minus 10% if no method of measurement is indicated.

The use of the term "or" in the claims is used to mean "and/or" unless explicitly indicated to refer to alternatives only or if the alternatives are mutually exclusive.

The terms "comprise", "have", "include" and "contain" (and their variants) are open-ended linking verbs and allow the addition of other elements when used in a claim.

The phrase "consisting of" is closed, and excludes all additional elements.

The phrase "consisting essentially of" excludes additional material elements, but allows the inclusions of non-material elements that do not substantially change the nature of the invention.

Any claim or claim element introduced with the open transition term "comprising," may also be narrowed to use the phrases "consisting essentially of" or "consisting of," and vice versa. However, the entirety of claim language is not repeated verbatim in the interest of brevity herein.

The following abbreviations may be used herein:

ABBREVIATION	TERM
API	American Petroleum Institute
BHP	bottom-hole pressure
CCE	Constant composition expansion, aka constant mass expansion (CME). The bubble point pressure is determined by an experiment called the CCE. The device used to perform this experiment is the PVT cell. CCE test is performed on a sample in a high pressure cell fitted with a glass window. In this test the cell pressure is reduced in steps and the pressure at which the first sign of gas bubbles is observed is recorded as bubble-point pressure for the oil samples and the first sign of liquid droplets is recorded as the dew-point pressure for the gas condensate samples.
FC-40	a commercial inert fluid used to store cores, also known as FLUORINERT ™ Not actually inert as it dissolves lighter hydrocarbons.
FID	Flame Ionization detector
GC	Gas chromatography
GOR	Gas to oil ratio
GTM	Gas transient model
HPHT	High pressure, high temperature—suitable for RTP conditions.
HPLC	High pressure liquid chromatography
P	Pressure
RTP	Reservoir Temperature & Pressure
STP	Standard Temperature & Pressure
TAN	Total acid number
TP	Temperature & Pressure
T	Temperature
PVT cell	A pressure, volume, temperature cell—a vessel capable of assay at RTP.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1.1**. CCE experiment on live oil at 303° F. Relative volume as a function of pressure.

FIG. **1.2**. CCE experiment on live oil at 303° F. Oil compressibility as a function of pressure.

FIG. **2.1**. CCE experiment of live oil/FC-40 fluid system at 303° F. Relative volume as a function of pressure.

FIG. **2.2**. CCE experiment of live oil/FC-40 fluid system at 303° F. Oil/FC-40 compressibility as a function of pressure.

FIG. **3**. PICTURE 1: Oil before contact with FC-40.

FIG. **4**. PICTURE 2: Initial contact with FC-40.

FIG. **5**. PICTURE 3: Oil/FC-40 initial interface (no mixing).

FIG. **6**. PICTURE 4: Oil/FC-40 dispersion layer (no mechanical mixing).

FIG. **7**. PICTURE 5: Oil/FC-40 dispersion layer **2** (no mechanical mixing).

FIG. **8**. PICTURE 6: Initiate mechanical mixing.

FIG. **9**. PICTURE 7: Oil/FC-40 interface fluid change during mechanical mixing.

FIG. **10**. PICTURE 8: Oil/FC-40 interface after aging overnight.

FIG. **11**. PICTURE 9: Oil/FC-40 interface at saturation pressure.

FIG. **12**. PICTURE 10: Oil/gas interface at saturation pressure.

FIG. **13**. PICTURE 11: FC-40 after flashing from cell.

DETAILED DESCRIPTION OF THE DISCLOSURE

To further advance our sealed cell development work, an experiment was devised to understand liquid and gas phase hydrocarbon solubilities in FC-40 (FLUORINERT™). Previous accepted industry standards for oil solubilities in FC-40 (e.g., none) were established at atmospheric temperature and pressure conditions. However, due to the nature of the sealed cell acquisition and laboratory procedures, FC-40, reservoir samples and associated hydrocarbons are in contact with each other at pressures and temperatures in great excess of those used to establish the original solubility standards. Thus, we suspected that the prior data is not accurate.

To understand the temperature and pressure impact on hydrocarbon solubilities in FC-40 a number of tests at RTP were conducted, as described below. In these experiments, Eagle Ford Hunsaker B9 live oil samples with reconditioned FC-40 fluid were studied at RTP of this play (5000 psia, 303° F.). In general, the live oil is characterized before and after equilibration with FC-540 or other test fluid, and changes in the characterization indicate that the test fluid is not inert. In particular, one might see changes in density, components, bubble point, dew point and the like. In this instance, we determined that FC-40 is not inert—solubilizing some of the lighter oil components and thus changing each of these parameters.

It is common to use recycled FC-40 in the coring apparatus due to the high expense of FC-40 and in reliance on the assumption that it is inert. Depending on the program, we have requested virgin FC-40 to be used, but our initial proof of concept work was performed with used FC-40. Preparing the FC-40 as described herein ensures if the experiment is undertaken with recycled fluids the full solubility of oil in the FC-40 is measured.

FC-40 fluid obtained from previous pressure core projects was subjected to vacuum and heat overnight to remove any previously solubilized hydrocarbon components. The FC-40 fluids from different core samples were combined and then analyzed for chemical constituency with gas chromatography with carbon disulfide (CS_2) solvent with an internal standard.

To obtain the composition of live oil, we flash to ambient conditions, measure the gas, the dead oil composition, and the gas to oil ratio (GOR) and calculate the live oil composition from that by adding the gas components back in. The

same can be done after equilibration of test fluid, such as FC-40, at RTP and the results compared to determine if the test fluid is indeed inert.

The bubble point pressure is determined by an experiment called the constant composition expansion or CCE. The CCE is done on the live oil before and after RTP equilibration with FC-40. If FC-40 is truly inert, the bubble point should not change. To perform a CCE, a known volume of live oil from a cylinder is transferred to a PVT cell. The live oil or live oil and FC-40 mixture are stabilized for 24 hours at RTP conditions. Then, an isothermal depressurization of at least 9 pressure steps is undertaken above saturation pressure. Below the bubble point pressure, a similar isothermal depressurization down to maximum expansion of the PVT cell volume is conducted. Cell volume is recorded at each pressure step. Saturation pressure is determined visually (herein we used bubble point) and graphically from the CCE experiment.

In more detail, these experiments are described as follows:

Fc-40 and Live Oil Mixture Study

The following experimental procedures were followed, and corresponding results are included herein:

1. Measure the composition of live oil (including weight % of the components) and density (HPHT densitometer) at 5000 psi and 303° F. (RTP).
2. Perform a CCE test to determine bubble point of live oil at RTP.
3. Flash the live oil and measure the density of the remaining oil.
4. Clean the cell and charge it with 310 cc of reconditioned FC-40 and 60-cc live oil.
5. Mix.
6. Equilibrate the mixture at RTP.
7. Measure the volume of the oil phase and FC-40 phase at RTP.
8. Perform another CCE experiment to determine bubble point of the equilibrated FC-40/oil system at RTP.
9. Displace the FC-40 and flash a portion of the remaining oil phase to STP or ambient conditions to measure amount and composition of gas that leaves solution.
10. Displace the remainder of the oil phase and measure density (HPHT densitometer) and composition of the oil at STP.

The reservoir fluid composition is reported in Table 1. It had a bubble point of 3547 psia at 303° F. (Table 2). Constant composition expansion at 303° F. indicated a fluid density of 0.5302 g/cc at the saturation pressure (bubble point) of 3547 psia (Table 3), and average total compressibility of 4.227×10^{-5} psi^{-1} (Table 4). Table 5 reports a constant composition expansion experiment performed on the reservoir fluid/FC-40 mix where a bubble point of 617 psia (shown in Table 6) at 303° F. was measured. The oil phase volume shrank from 60 cc at 5015 psig to 20.30 cc after mixing. FIG. **4-7** (Pictures 2-5) show the rapid diffusion of the oil into the FC-40 phase before mixing.

The 20.3 cc of oil remaining was displaced and its composition measured as reported in Table 7. The FC-40 was displaced and flashed to ambient conditions; a gas phase was recovered and its composition measured and an oil phase that separated from the FC-40 also had its composition determined.

The composition of the oil components that solubilized into the FC-40 was estimated in Table 8 by combining the gas and oil phases that came out of the FC-40 at ambient conditions by material balance. The material balance around the entire experiment (Table 9) indicates that the live oil

composition reported in Table 8 should have more light ends. This is probably due to the fact that light hydrocarbons have significant solubility in FC-40 even at atmospheric conditions. FIG. **13** confirms that the light hydrocarbons are more soluble in FC-40, leaving the heavier components in the oil phase.

Since the current standard so-called "inert" fluid (FC-40) (Table 10) removes light hydrocarbons, it would be beneficial to find a better inert fluid for downhole uses at RTP. The ideal fluid should be dense, and inert to hydrocarbons, as well as not preferentially solubilize any of the hydrocarbon components. In addition, the solution should be reasonably safe to use, and not contribute to environmental degradation or present safety hazards.

To that end, we will test silicon-based molecules that are fully substituted with fluorine, or silicon-based compounds with hydrophobic R groups, including siloxanes (SiH_3 ($OSiH_2$)nOSiH$_3$), or silicones.

Silicone fluids can be discussed in two categories: inert fluids and functional fluids. Polydialkyl-, arylalkyl- and fluoroalkylsiloxane polymers and co-polymers, carrying no reactive (under-the-use conditions) groups, belong to the first category and may be tested as described herein.

A possible test fluid is $(CH_3)_3$—Si—O—$Si(CH_3)_2$—O—$Si(CH_3)(R)$—O—$Si(CH_3)_3$ where (R) is hydrophobic.

Another test fluid might be a fluorosyl:


where c = 2-5
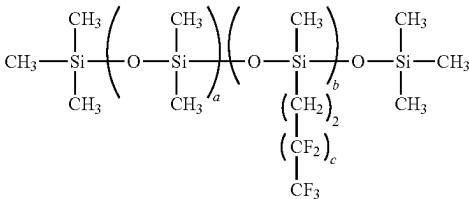
In fact, many fluorosyls are available for testing herein, including Fluorosil 2010, Fluorosil H418, Fluorosil J15, Fluorosil L118, Fluorosil OH C7-F, Silwax F, Fluorosil OH ACR C7-F, Fluorosil TFP 1000, Fluorosil TFP 10,000, Fluorosil TFP D7, and the like.

High Temperature Silicones such as Dynalene 600 or SYLTHERM (a polydimethylsiloxane liquid) may also be tested.

Another option is phenylsiloxane-dimethylsiloxane copolymer and diphenylsiloxane-dimethylsiloxane copolymers. As phenyl groups replace methyl groups in a polysiloxane, several changes occur. Oxidation resistance, thermal stability, and shear resistance are enhanced.

Modified silicones that have a higher density and chemical resistance and are potential candidates include:
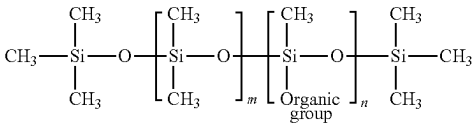
Modifcation type	Organic group	Product name	Viscosity (25° C.) [mm/s]	Specific gravity (25° C.)	Refractive Index (25° C.)	Features
Fluoroalkyl	—$CH_2CH_2CF_3$	FL-5	120	0.99	1.400	Good lubricity
		X-22-821	120	1.09	1.390	Chemical
		X-22-822	100	1.15	1.384	resistance
		FL-100-100cs	100	1.23	1.379	Oil &
		FL-100-450cs	450	1.28	1.381	solvent
		FL-100-1,000cs	1,000	1.28	1.381	resistance
		FL-100-10,000cs	10,000	1.30	1.382	High specific gravity Poor solubility Good releasability

Polyether-modified						
Modification type	Organic group	Product Name	Viscosity (25° C.) [mm/s]	Specific gravity (25° C.)	Refractive index (25°C.)	HLB	Features
Polyether	—$R(C_2H_4O)_a(C_3H_6O)_bR'$	KF-351A	70	1.06	1,450	12	Water
		KF-352A	1,600	1.03	1,446	7	soluble
		KF-353	430	1.04	1,438	10	Water
		KF-354L	200	1.10	1,463	16	dispersible
		KF-355A	150	1.07	1,453	12	Easily
		KF-615A	920	1.05	1,451	10	emulsifable
		KF-945	130	1.00	1,420	4	Low
		KF-640	20	1.01	1,444	14	surface
		KF-642	50	1.04	1,443	12	tension
		KF-643	19	1.01	1,442	14	Good
		KF-644	38	1.02	1,446	11	permeability
		KF-6020	180	1.00	1,417	4	Anti-
		KF-6204	70	1.05	1,451	10	fogging
		X-22-4515	4,000	1.03	1,445	5	property

-continued

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - O \left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - O \right]_m \left[\underset{\underset{\substack{Organic \\ group}}{|}}{\overset{\overset{CH_3}{|}}{Si}} - O \right]_n \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - CH_3$$

Polyether (odortest)	$-R(C_2H_4O)_a(C_3H_6O)_bR'$		KF-6011	130	1.07	1,450	12	Compatibility
			KF-6012	1,500	1.03	1,448	7	
			KF-6015	130	1.00	1,419	5	
			KF-6017	530	1.01	1,420	5	

Phenyl-modified

Modification type	Organic group	Product name	Viscosity (25° C.) [mm/s]	Specific gravity (25° C.)	Refractive index (25° C.)	Features
Phenyl	$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - O \left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - O \right]_m \left[\underset{\underset{C_6H_5}{|}}{\overset{\overset{C_6H_5}{|}}{Si}} - O \right]_n \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - CH_3$	KF-50-100cs	100	0.995	1.427	Heat resistance
		KF-50-300cs	300	0.996	1.427	High refractive
		KF-50-1,000cs	1,000	1.00	1.427	index
		KF-50-3,000cs	3,000	1.00	1.427	Compatibility
		KF-53	170	1.06	1.485	Low-temperature
		KF-54	400	1.07	1.505	resistance
		X-21-3265	400	1.07	1.505	
		KF-54SS	500	1.07	1.504	

Brominated hydrocarbons may also work, and mercury compounds or mercury containing mixes in the manner similar to that described herein. Any of the above described or similar compounds that test as inert in the herein described tests will be used as core sampling inert fluids and/or core storage inert fluids.

Suitable compounds may not be 100% inert, but the ideal solution would be 95% inert or better for the time it takes to collect core samples and test them—e.g., no more than 5% change in content. Thus, the inert fluid should be at least 95% inert when tested with core at RTP for at least 6 hours, preferably at least 12, or even 24, 36 or 48 hours. Even more preferred is a 96, 97, 98, or 99% inertness.

TABLE 1

		Flashed Gas	Flashed Oil				Reservoir Fluid	
Component		Mole %	Mole %	Wt %	Molecular Weight	Specific Gravity	Mole %	Wt %
Nitrogen	N_2	0.237	0.000	0.000	28.01	0.8100	0.171	0.067
Carbon Dioxide	CO_2	1.028	0.000	0.000	44.01	0.8270	0.741	0.458
Hydrogen Sulphide	H_2S	0.000	0.000	0.000	34.08	0.7960	0.000	0.000
Methane	C_1	68.722	0.074	0.006	16.05	0.3000	49.593	11.181
Ethane	C_2	14.516	0.325	0.051	30.07	0.3560	10.562	4.461
Propane	C_3	8.004	0.701	0.161	44.10	0.5010	5.969	3.698
i-Butane	$i-C_4$	1.340	0.326	0.099	58.12	0.5570	1.057	0.863
n-Butane	$n-C_4$	2.879	1.365	0.413	58.12	0.5790	2.457	2.006
i-Pentane	$i-C_5$	1.190	1.426	0.535	72.15	0.6200	1.256	1.273
n-Pentane	$n-C_5$	0.990	2.217	0.832	72.15	0.6260	1.332	1.350
Hexanes	C_6	0.708	5.727	2.504	84.00	0.6900	2.106	2.486
Heptanes	C_7	0.182	8.002	3.957	95.00	0.7270	2.361	3.151
Octanes	C_8	0.106	10.632	5.921	107.00	0.7490	3.039	4.568
Nonanes	C_9	0.091	9.451	5.952	121.00	0.7680	2.699	4.588
Decanes	C_{10}	0.007	7.451	5.274	136.00	0.7820	2.081	3.977
Undecanes	C_{11}	0.000	5.945	4.611	149.00	0.7930	1.657	3.467
Dodecanes	C_{12}	0.000	4.796	4.069	163.00	0.8040	1.337	3.060
Tridecanes	C_{13}		4.593	4.207	176.00	0.8150	1.280	3.164
Tetradecanes	C_{14}		3.952	3.929	191.00	0.8260	1.101	2.955
Pentadecanes	C_{15}		3.579	3.856	207.00	0.8360	0.997	2.900
Hexadecanes	C_{16}		2.906	3.343	221.00	0.8430	0.810	2.514
Heptadecanes	C_{17}		2.617	3.228	237.00	0.8510	0.729	2.428
Octadecanes	C_{18}		2.468	3.199	249.00	0.8560	0.688	2.406
Nonadecanes	C_{19}		2.301	3.125	261.00	0.8610	0.641	2.350
Eicosanes	C_{20}		1.897	2.715	275.00	0.8660	0.529	2.042
Heneicosanes	C_{21}		1.718	2.584	289.00	0.8710	0.479	1.943
Docosanes	C_{22}		1.485	2.342	303.00	0.8760	0.414	1.761
Tricosanes	C_{23}		1.354	2.234	317.00	0.8810	0.377	1.680
Tetracosanes	C_{24}		1.220	2.102	331.00	0.8850	0.340	1.581
Pentacosanes	C_{25}		1.086	1.949	345.00	0.8880	0.302	1.466
Hexacosanes	C_{26}		1.011	1.890	359.00	0.8920	0.282	1.421

TABLE 1-continued

Heptacosanes	C_{27}	0.914	1.775	373.00	0.8960	0.255	1.335
Octacosanes	C_{28}	0.834	1.680	387.00	0.8990	0.232	1.264
Nonacosanes	C_{29}	0.750	1.562	400.00	0.9020	0.209	1.174
Tricontanes	C_{30}	0.665	1.436	415.00	0.9050	0.185	1.080
Hentriacontanes	C_{31}	0.579	1.292	429.00	0.9090	0.161	0.972
Dotriacontanes	C_{32}	0.550	1.269	443.00	0.9120	0.153	0.955
Tritriacontanes	C_{33}	0.499	1.187	457.00	0.9150	0.139	0.893
Tetratriacontanes	C_{34}	0.488	1.197	471.00	0.9170	0.136	0.900
Pentatriacontanes	C_{35}	0.404	1.020	485.00	0.9200	0.113	0.767
Hexatriacontanes plus	C36+	3.693	12.494	650.00	0.9913	1.029	9.396
		100.00	100.00			100.00	100.00
Molecular Weight	24.47		192.13				71.19

Compositional Grouping and Plus Fraction Properties

Group	Mol %	wt %	MW	Density
C7+	24.76	72.16	207.49	0.8461
C12+	12.92	52.41	255.79	0.8758
C20+	5.34	30.63	408.67	0.9195
C30+	1.92	14.96	555.73	0.9605
C36+	1.03	9.40	650.00	0.9913

TABLE 2

Main PVT Results

TEST CONDITIONS

Pressure	5000 psia
Temperature	303.0 F.

CONSTANT COMPOSITION EXPANSION @ 303.0 F.

Saturation Pressure (Bubble Point)	3547.31 psia
Compressibility @ Saturation Pressure	4.2274E−05 psia^{-1}

SEPARATOR FLUID FLASH TEST TO AMBIENT CONDITIONS

At Saturation Pressure

Oil Formation Volume Factor	2.0052 res.bbl/STB
Flash Gas-Oil Ratio	1432.89 scf/STB

At Tank Conditions

Residual Oil Density	0.7996 g/cm^3
API Gravity	45.47
Measured MW	195.30

Cylinder Number: 832808

Volume of oil left: 300 cc at 5000 psi and 303 F.

TABLE 3

Constant Composition Expansion @ 303.0 F.

Pressure (psia)	RelativeVolume [1]	Y-Fuaction [2]	Fluid Density (g/cc) [3]	Liquid Volume Vliq/Vb %
7015	0.9059		0.5853	
6515	0.9146		0.5797	
6015	0.9244		0.5736	
5515	0.9354		0.5668	
5015	0.3480		0.5593	
4515	0.9627		0.5598	
4015	0.9862		0.5409	
3547 Psat	1.0000		0.5302	100.000
3379	1.0251	1.9791		94.430
3211	1.6541	1.9339		90.836
3043	1.0877	1.8886		88.819
2875	1.1268	1.8434		85.321
2707	1.1725	1.7982		82.849
2539	1.2265	1.7530		89.754
2371	1.2964	1.7077		78.589
2293	1.3669	1.6625		76.583

TABLE 3-continued

Constant Composition Expansion @ 303.0 F.

Pressure (psia)	RelativeVolume [1]	Y-Fuaction [2]	Fluid Density (g/cc) [3]	Liquid Volume Vliq/Vb %
2935	1.4593	1.6173		74.507
1867	1.5723	1.5721		72.604
1599	1.7123	1.5268		70.898
1531	1.8886	1.4816		69.257
1363	2.1153	1.4364		67.744
1195	2.4144	1.3912		65.998
1027	2.8225	1.3459		64.600

[1] Volume at indicated pressure per volume at saturation pressure
[2] Y Function = ((Psat − P)/P)(Relative Volume − 1)
[3] Measured by HPHT densfometer
Psat—Saturation Pressure

TABLE 4

Constant Composition Expansion @ 303.0 F.
Oil Compressibility as a Function of Pressure

Pressure Range		Average Total Compressibility (psi^{-1})
From (psia)	To (psia)	
7015	6515	1.903E−05
6515	6015	2.111E−05
6015	5515	2.357E−05
5515	5015	2.657E−05
5015	4515	3.049E−05
4515	4015	3.579E−05
4015	3547 Psat	4.227E−05

TABLE 5

Constant Composition Expansion of Live Oil/FC-40 Fluid System @ 303.0 F.

Pressure (psia)	Total Volume cc	Relative Volume [1]	Y-Function [2]	Gas Phase Volume cc	Oil Phase Volume cc
5015	374.01	0.8822			20.30
4015	380.25	0.8969			20.61

TABLE 5-continued

Constant Composition Expansion of Live Oil/FC-40 Fluid System @ 303.0 F.

Pressure (psia)	Total Volume cc	Relative Volume [1]	Y-Function [2]	Gas Phase Volume cc	Oil Phase Volume cc
3015	387.90	0.9149			20.64
2515	392.72	0.9263			20.54
2015	398.36	0.9396			20.54
1515	405.22	0.9558			20.59
1015	414.00	0.9765			20.67
617 Psat	423.96	1.0000		0.0000	20.05
606	427.51	1.0084	2.165	6.444	19.79
595	431.73	1.0183	2.017	9.485	19.51
584	435.99	1.0284	1.991	13.961	19.23
573	446.30	1.0385	1.992	20.549	18.96
562	445.19	1.0501	1.954	28.527	18.78
551	451.63	1.0653	1.835	33.881	18.86
540	458.16	1.0807	1.767	40.240	18.93
529	464.79	1.0963	1.727	47.793	19.01
516	471.51	1.1122	1.704	56.762	19.08
507	478.70	1.1291	1.680	63.983	19.29
496	486.12	1.1466	1.664	70.907	19.55
485	493.67	1.1644	1.655	78.580	19.81
474	501.32	1.1825	1.653	87.084	20.07
463	508.66	1.1998	1.665	95.880	20.00
452	514.58	1.2138	1.708	103.248	18.80

TABLE 5-continued

Constant Composition Expansion of Live Oil/FC-40 Fluid System @ 303.0 F.

Pressure (psia)	Total Volume cc	Relative Volume [1]	Y-Function [2]	Gas Phase Volume cc	Oil Phase Volume cc
Loading Information (5000 psig & 303° F.)					
Reservoir Oil, cc				60.00	
FC-40, cc				314.01	

[1] Volume at indicated pressure per volume at saturation pressure
[2] Y Function = (Psat − P)/P)/(Relative Volume − 1)
Psat—Saturation Pressure

TABLE 6

Constant Composition Expansion of Live Oil/FC-40 Fluid System @ 303.0 F. Live Oil/ FC-40 Fluid System Compressibility as a Function of Pressure

Pressure Range		Average Total
From (psia)	To (psia)	Compressibility (psi^{-1})
5015	4015	1.655E−05
4015	3015	1.991E−05
3015	2515	2.468E−05
2515	2015	2.854E−05
2015	1515	3.417E−05
1515	1015	4.286E−05
1015	617 Psat	5.971E−05

TABLE 7

Displaced Oil Phase Composition (After mixing with FC-40 in the PVT cell)

Component		Flashed Gas Mole %	Flashed Oil Mole %	Flashed Oil Wt %	Molecular Weight	Specific Gravity	Oil Phase Mole %	Oil Phase Wt %
Nitrogen	N_2	2.910	0.000	0.000	28.01	0.8100	0.686	0.089
Carbon Dioxide	CO_2	0.805	0.000	0.000	44.01	0.8270	0.190	0.038
Hydrogen Sulphide	H_2S	0.000	0.000	0.000	34.08	0.7960	0.000	0.000
Methane	C_1	66.763	0.015	0.001	16.05	0.3000	15.742	1.165
Ethane	C_2	16.474	0.191	0.021	30.07	0.3560	4.028	0.559
Propane	C_3	8.075	0.651	0.104	44.10	0.5010	2.400	0.488
i-Butane	$i\text{-}C_4$	1.050	0.290	0.061	58.12	0.5570	0.469	0.126
n-Butane	$n\text{-}C_4$	2.180	1.035	0.218	58.12	0.5790	1.304	0.350
i-Pentane	$i\text{-}C_5$	0.603	0.772	0.201	72.15	0.6200	0.732	0.244
n-Pentane	$n\text{-}C_5$	0.572	1.109	0.290	72.15	0.6260	0.983	0.327
Hexanes	C_6	0.392	2.377	0.722	84.00	0.6900	1.909	0.739
Heptanes	C_7	0.110	3.547	1.219	95.00	0.7270	2.737	1.199
Octanes	C_8	0.045	6.466	2.503	107.00	0.7490	4.953	2.444
Nonanes	C_9	0.018	4.824	2.111	121.00	0.7680	3.691	2.060
Decanes	C_{10}	0.002	4.317	2.124	136.00	0.7820	3.301	2.070
Undecanes	C_{11}	0.000	3.864	2.083	149.00	0.7930	2.954	2.029
Dodecanes	C_{12}	0.000	3.538	2.086	163.00	0.8040	2.705	2.033
Tridecanes	C_{13}		3.785	2.410	176.00	0.8150	2.893	2.348
Tetradecanes	C_{14}		3.645	2.519	191.00	0.8260	2.786	2.454
Pentadecanes	C_{15}		3.675	2.752	207.00	0.8360	2.809	2.681
Hexadecanes	C_{16}		3.332	2.664	221.00	0.8430	2.547	2.596
Heptadecanes	C_{17}		3.256	2.791	237.00	0.8510	2.488	2.720
Octadecanes	C_{18}		3.275	2.950	249.00	0.8560	2.504	2.875
Nonadecanes	C_{19}		3.338	3.152	261.00	0.8610	2.552	3.071
Eicosanes	C_{20}		2.984	2.969	275.00	0.8660	2.281	2.893
Heneicosanes	C_{21}		2.884	2.584	289.00	0.8710	2.205	2.938
Docosanes	C_{22}		2.655	2.910	303.00	0.8760	2.029	2.835
Tricosanes	C_{23}		2.556	2.931	317.00	0.8810	1.954	2.856
Tetracosanes	C_{24}		2.422	2.900	331.00	0.8850	1.852	2.826
Pentacosanes	C_{25}		2.252	2.811	345.00	0.8880	1.722	2.739
Hexacosanes	C_{26}		2.186	2.839	359.00	0.8920	1.671	2.766

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TABLE 7-continued

Component							
Heptacosanes	C_{27}	2.053	2.770	373.00	0.8960	1.569	2.699
Octacosanes	C_{28}	1.925	2.695	387.00	0.8990	1.472	2.626
Nonacosanes	C_{29}	1.775	2.569	400.00	0.9020	1.357	2.503
Tricontanes	C_{30}	1.649	2.476	415.00	0.9050	1.260	2.412
Hentriacontanes	C_{31}	1.458	2.263	429.00	0.9090	1.114	2.205
Dotriacontanes	C_{32}	1.426	2.285	443.00	0.9120	1.090	2.226
Tritriacontanes	C_{33}	1.297	2.144	457.00	0.9150	0.992	2.089
Tetratriacontanes	C_{34}	1.294	2.204	471.00	0.9170	0.989	2.148
Pentatriacontanes	C_{35}	1.175	2.062	485.00	0.9200	0.898	2.009
Hexatriacontanes plus	C_{36+}	10.706	25.174	650.00	0.9913	8.183	24.528
		100.00	100.00			100.00	100.00
Calculated MW		23.63	276.43				216.86

Compositional Grouping and Plus Fraction Properties

Group	Mol %	wt %	MW	Density
C7+	71.56	95.88	290.57	0.8882
C12+	53.92	86.07	324.97	0.8985
C20+	32.64	65.30	433.88	0.9280
C30+	14.53	37.62	561.56	0.9625
C36+	8.18	24.53	650.00	0.9913

Zero Flash Results (5000 psig & 303 F.)

Live oil density, g/cc	0.8883
GOR, scf/stb	125.02
Flashed oil density, g/cc	0.8429
Flashed oil MW	287.60

TABLE 8

Oil Phase in Solution in FC-40 Composition (After mixing with FC-40 in the PVT cell)

Component		Flashed Gas Mole %	Flashed Oil Mole %	Flashed Oil Wt %	Molecular Weight	Specific Gravity	Live Oil* Mole %	Live Oil* Wt %
Nitrogen	N_2	0.986	0.000	0.000	28.01	0.8100	0.851	0.568
Carbon Dioxide	CO_2	1.017	0.000	0.000	44.01	0.8270	0.877	0.920
Hydrogen Sulphide	H_2S	0.000	0.000	0.000	34.08	0.7960	0.000	0.000
Methane	C_1	69.727	0.015	0.002	16.05	0.3000	60.150	22.996
Ethane	C_2	14.149	0.132	0.026	30.07	0.3560	12.223	8.756
Propane	C_3	7.522	0.526	0.149	44.10	0.5010	6.561	6.893
i-Butane	$i\text{-}C_4$	1.181	0.327	0.122	58.12	0.5570	1.064	1.473
n-Butane	$n\text{-}C_4$	2.536	1.325	0.496	58.12	0.5790	2.372	3.284
i-Pentane	$i\text{-}C_5$	0.943	1.391	0.646	72.15	0.6200	1.004	1.726
n-Pentane	$n\text{-}C_5$	0.858	2.105	0.978	72.15	0.6260	1.029	1.769
Hexanes	C_6	0.703	5.548	3.000	84.00	0.6900	1.369	2.739
Heptanes	C_7	0.228	8.537	5.220	95.00	0.7270	1.370	3.100
Octanes	C_8	0.104	16.177	11.142	107.00	0.7490	2.312	5.894
Nonanes	C_9	0.031	11.577	9.017	121.00	0.7680	1.617	4.662
Decanes	C_{10}	0.009	9.473	8.293	136.00	0.7820	1.309	4.242
Undecanes	C_{11}	0.003	7.563	7.254	149.00	0.7930	1.042	3.697
Dodecanes	C_{12}	0.000	5.865	6.154	163.00	0.8040	0.806	3.129
Tridecanes	C_{13}		5.296	6.000	176.00	0.8150	0.728	3.051
Tetradecanes	C_{14}		4.225	5.194	191.00	0.8260	0.580	2.641
Pentadecanes	C_{15}		3.555	4.736	207.00	0.8360	0.488	2.408
Hexadecanes	C_{16}		2.653	3.773	221.00	0.8430	0.364	1.919
Heptadecanes	C_{17}		2.208	3.368	237.00	0.8510	0.303	1.712
Octadecanes	C_{18}		1.936	3.103	249.00	0.8560	0.266	1.578
Nonadecanes	C_{19}		1.665	2.797	261.00	0.8610	0.229	1.422
Eicosanes	C_{20}		1.264	2.237	275.00	0.8660	0.174	1.137
Heneicosanes	C_{21}		1.058	1.968	289.00	0.8710	0.145	1.001
Docosanes	C_{22}		0.840	1.639	303.00	0.8760	0.115	0.833
Tricosanes	C_{23}		0.710	1.449	317.00	0.8810	0.098	0.737
Tetracosanes	C_{24}		0.589	1.255	331.00	0.8850	0.081	0.638
Pentacosanes	C_{25}		0.463	1.074	345.00	0.8880	0.066	0.546
Hexacosanes	C_{26}		0.414	0.957	359.00	0.8920	0.057	0.487
Heptacosanes	C_{27}		0.353	0.848	373.00	0.8960	0.049	0.431
Octacosanes	C_{28}		0.289	0.719	387.00	0.8990	0.040	0.366
Nonacosanes	C_{29}		0.250	0.644	400.00	0.9020	0.034	0.327
Tricontanes	C_{30}		0.212	0.566	415.00	0.9050	0.029	0.288
Hentriacontanes	C_{31}		0.159	0.440	429.00	0.9090	0.022	0.224
Dotriacontanes	C_{32}		0.153	0.437	443.00	0.9120	0.021	0.222

TABLE 8-continued

Oil Phase in Solution in FC-40 Composition (After mixing with FC-40 in the PVT cell)							
Tritriacontanes	C_{33}	0.129	0.379	457.00	0.9150	0.018	0.193
Tetratriacontanes	C_{34}	0.120	0.365	471.00	0.9170	0.017	0.186
Pentatriacontanes	C_{35}	0.106	0.332	485.00	0.9200	0.015	0.169
Hexatriacontanes plus	C_{36+}	0.770	3.220	650.00	0.9913	0.106	1.637
		100.00	100.00			100.000	100.000
Calculated MW		23.92	155.35			41.978	

*Estimated based on mass balance calculation.

Compositional Grouping and Plus Fraction Properties				
Group	Mol %	wt %	MW	Density
C7+	12.50	48.88	164.13	0.8116
C12+	4.85	27.28	205.31	0.8465
C20+	1.09	9.42	364.35	0.9026
C30+	0.23	2.92	540.45	0.9549
C36+	0.11	1.64	650.00	0.9913

Zero Flash Results (5000 psig & 303 F.)	
GLR*, scf/stb	152.40
Flashed liquid density*, g/cc	1.8500

*Liquid is mixture of live oil and FC-40
*FC-40 fluid density at STP

TABLE 9

Material Balance Calculation Basis for Table 8		
INITIAL VOLUMETRIC CONDITIONS		
Pressure:	5015 psia	
Temperature:	303.0 F.	
Reservoir fluid volume:	60.00 cc	0.4714 mole
Reservoir fluid density:	0.5593 g/cc	
Displaced oil volume:	20.30 cc	0.0832 mole
Displaced oil density:	0.8883 g/cc	
Oil phase in solution + FC-40:	353.71 cc	0.3882 mole
OIL PHASE IN SOLUTION + FC-40 FLASH TEST VOLUMETRICS		
Total flashed volume:	20.84 cc	5015 psia & 303 F.
Gas volume collected:	467.51 cc	14.696 psia & 60 F.
Totas Gas in solution (scaled)	7933.78 cc	0.3349 mole
Dead oil in solution by material balance		0.0533 mole

TABLE 10

FC-40 Preparation					
		Composition			
Component		Mole %	Wt %	Molecular Weight	Specific Gravity
Nitrogen	N_2	0.000	0.000	28.01	0.8100
Carbon Dioxide	CO_2	0.000	0.000	44.01	0.8270
Hydrogen Sulphide	H_2S	0.000	0.000	34.08	0.7960
Methane	C_1	0.000	0.000	16.05	0.3000
Ethane	C_2	0.042	0.017	30.07	0.3560
Propene	C_3	0.033	0.019	44.10	0.5010
i-Butane	$i\text{-}C_4$	0.000	0.000	58.12	0.5570
n-Butane	$n\text{-}C_4$	0.000	0.000	58.12	0.5790
i-Pentane	$i\text{-}C_5$	0.000	0.000	72.15	0.6200
n-Pentane	$n\text{-}C_5$	0.000	0.000	72.15	0.6260
Carbon Disulfide	CS_2	99.910	99.944	76.13	n/a
Hexanes	C_6	0.000	0.000	84.00	0.6900
Heptanes	C_7	0.000	0.000	95.00	0.7270
Octanes	C_8	0.016	0.020	107.00	0.7490
Nonanes	C_9	0.000	0.000	121.00	0.7680
Decanes	C_{10}	0.000	0.000	136.00	0.7820

TABLE 10-continued

FC-40 Preparation					
		Composition			
Component		Mole %	Wt %	Molecular Weight	Specific Gravity
Undecanes	C_{11}	0.000	0.000	149.00	0.7930
Dodecanes	C_{12}	0.000	0.000	163.00	0.8040
Tridecanes	C_{13}	0.000	0.000	176.00	0.8150
Tetradecanes	C_{14}	0.000	0.000	191.00	0.8260
Pentadecanes	C_{15}	0.000	0.000	207.00	0.8360
Hexadecanes	C_{16}	0.000	0.000	221.00	0.8430
Heptadecanes	C_{17}	0.000	0.000	237.00	0.8510
Octadecanes	C_{18}	0.000	0.000	249.00	0.8560
Nonadecanes	C_{19}	0.000	0.000	261.00	0.8610
Eicosanes	C_{20}	0.000	0.000	275.00	0.8660
Heneicosanes	C_{21}	0.000	0.000	289.00	0.8710
Docosanes	C_{22}	0.000	0.000	303.00	0.8760
Tricosanes	C_{23}	0.000	0.000	317.00	0.8810
Tetracosanes	C_{24}	0.000	0.000	331.00	0.8850
Pentacosanes	C_{25}	0.000	0.000	345.00	0.8880
Hexacosanes	C_{26}	0.000	0.000	359.00	0.8920
Heptacosanes	C_{27}	0.000	0.000	373.00	0.8960
Octacosanes	C_{28}	0.000	0.000	387.00	0.8990
Nonacosenes	C_{29}	0.000	0.000	400.00	0.9020
Tricontanes	C_{30}	0.000	0.000	415.00	0.9050
Hentriacontanes	C_{31}	0.000	0.000	429.00	0.9090
Dotriacontanes	C_{32}	0.000	0.000	443.00	0.9120
Tritriacontanes	C_{33}	0.000	0.000	457.00	0.9150
Tetatriacontanes	C_{34}	0.000	0.000	471.00	0.9170
Pentatriacontanes	C_{35}	0.000	0.000	485.00	0.9200
Hexatriacontanes plus	C_{36+}	0.000	0.000	650.00	0.9913
		100.00	100.00		

Weight of Sample Used	0.8401	g
Internal Standard Added	0.0095	g

The invention claimed is:

1. A method of assaying a test fluid for collecting reservoir core samples at reservoir temperature and pressure (RTP) and determining if said test fluid is inert at RTP, said method comprising:

a) assaying a live oil to generate a first dataset using methods comprising at least one of:

i) determining a weight contribution of components of said live oil;

ii) determining a bubble point of said live oil;

iii) determining a density of a remaining oil when said live oil is flashed to standard temperature and pressure (STP) or ambient conditions;

iv) determining a weight contribution of gaseous components flashed from said live oil; or

v) determining total acid number (TAN), metal content, viscosity, asphaltene content, C7 content, nitrogen content, water content, carbon content, total contents, wax content, carbon residue content, conductivity, pour point, density at 15° C., salt content, sediment content, specific gravity, light end hydrocarbon content, mercaptan content, hydrogen content, total sulfur, hydrogen sulfide content or vapor pressure of said hydrocarbon phase or said remaining hydrocarbon phase;

b) assaying said live oil plus a test fluid mixed together and equilibrated at RTP to form hydrocarbon phase and a test fluid phase to generate a second dataset, using methods comprising at least one of:

i) determining a bubble point of said hydrocarbon phase;

ii) determining a weight contribution of components of said hydrocarbon phase;

iii) determining a density of a remaining hydrocarbon phase when said hydrocarbon phase is flashed to STP or ambient conditions;

iv) determining a weight contribution of gaseous components flashed from said hydrocarbon phase; or

v) determining total acid number (TAN), metal content, viscosity, asphaltene content, C7 content, nitrogen content, water content, carbon content, total contents, wax content, carbon residue content, conductivity, pour point, density at 15° C., salt content, sediment content, specific gravity, light end hydrocarbon content, mercaptan content, hydrogen content, total sulfur content, hydrogen sulfide content or vapor pressure of said hydrocarbon phase or said remaining hydrocarbon phase;

c) comparing said first dataset and said second dataset, wherein changes in said second dataset compared with said first dataset indicates that said test fluid is not inert, but no changes indicates said test fluid is inert and can be used to collect reservoir core samples at RTP.

2. The method of claim 1, wherein the weight contribution is determined with gas chromatography.

3. The method of claim 1, wherein the weight contribution of components of any fluid is determined with elemental composition and gas chromatography.

4. The method of claim 1, wherein the weight contribution of gaseous components is determined with gas chromatography.

5. The method of claim 1, wherein the weight contribution of components of any fluid is determined with elemental composition and gas chromatography with flame ionization detector (GC/FID).

6. The method of claim 1, wherein the density is determined using a High Pressure High Temperature (HPHT) densitometer at RTP.

7. The method of claim 1, wherein the bubble point is determined by stepping down the pressure from RTP and observing a pressure at which bubbles appear.

8. The method of claim 1, wherein the bubble point is determined by ASTM D2889-95 (2019).

9. The method of claim 1, wherein the RTP is an average temperature and pressure of a play in the reservoir.

10. The method of claim 1, wherein step a) and step b) assaying includes characterization of elements, C1-C40 components, the bubble point and the density.

11. The method of claim 10, wherein said characterization of elements and C1-C40 components are determined with elemental composition and gas chromatography.

12. The method of claim 10, wherein said characterization of elements and C1-C40 components are determined by elemental composition and gas chromatography with flame ionization detector (GC/FID).

13. The method of claim 10, wherein the density is determined using a High Pressure High Temperature (HPHT) densitometer at RTP.

14. The method of claim 10, wherein the bubble point is determined by stepping down a pressure from RTP and observing a pressure at which bubbles form.

15. The method of claim 10, wherein the bubble point is determined by ASTM D2889-95 (2019).

16. The method of claim 10, wherein the RTP is an average temperature and pressure of a play in the reservoir.

17. The method of claim 1, wherein step a) and step b) include assaying a composition, the density at 15° C., and the bubble point.

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