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(57) **Abstract**: Contrast agents and methods for use in geological applications are provided. Contrast agents can be a nanopolymorph material, such as titania nanotubes, and have a low-frequency dielectric permittivity. Methods of identifying one or more subterranean features during geological exploration are provided. Methods of identifying a ganglion of bypassed oil are provided. Methods of illuminating subterranean fractures in hydraulic fracturing are provided.

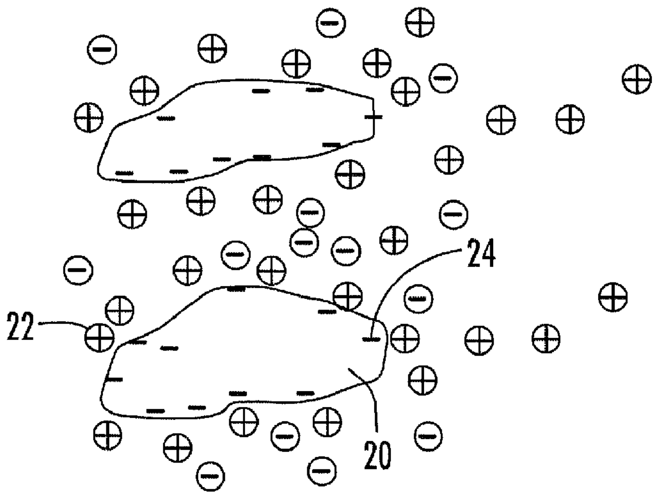

FIG. 1

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DESCRIPTION

DIELECTRIC CONTRAST AGENTS AND METHODS

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of and priority to U.S. Provisional Patent Application Serial No. 61,689,179, filed May 31, 2012, the disclosure of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

This presently disclosed subject matter relates generally to dielectric contrast agents or compositions and related methods and uses thereof. More specifically, the presently disclosed subject matter is directed to contrast agents or compositions and methods of use, for example and without limitation, in geological exploration, mining and the recovery of natural resources.

BACKGROUND

Geological exploration, mining and the recovery of natural resources require an ability to locate and define as best as possible reservoirs of natural resources, such as oil and natural gas. Currently available methods for identifying and estimating the quantity of oil and natural gas in a given location have limitations. Further, traditional methods of extracting oil and natural gas can be inefficient, thereby causing significant portions of oil and natural gas to remain unrecovered.

SUMMARY

It is an object of the subject matter disclosed herein to provide novel contrast agents and methods of use in geological exploration, mining and recovery.

An object of the presently disclosed subject matter having been stated hereinabove, and which is achieved in whole or in part by the subject matter disclosed herein and/or in the accompanying materials, this and other objects will become evident as the description proceeds when taken in connection with the accompanying drawings as best described hereinbelow.

BRIEF DESCRIPTION OF THE DRAWINGS

The features and advantages of the present subject matter will be more readily understood from the following detailed description which should be read in conjunction with the accompanying drawings that are given merely by way of explanatory and non-limiting example, and in which:

Figure 1 is a diagram illustrating clay or titanium oxide (TiO_2) double-layer polarization at the particle level;

Figures 2A and 2B are schematic illustrations illustrating contrast agents and their use to illuminate oil ganglions;

Figure 3 is a graphical representation comparing the dielectric enhancement of Bentonite clay and titanium nanotube (TiNT) as a function of frequency. Bentonite was tested at 5 wt% (long dashed line) and 10 wt% (short dashed line), while TiNT was tested at 10 wt% (dotted line) and 15 wt% (dashed and dotted line). NaCl (solid line) solution was used as a control;

Figure 4 is a schematic representation illustrating contrast agents encapsulated with a sensing membrane that is activated upon encountering an environmental stimulus;

Figures 5A and 5B are images of TiNTs. Figure 5A is a transmission electron microscopy (TEM) image of as-synthesized TiNTs. Figure 5B is a scanning electron microscopy (SEM) image of TiNTs;

Figure 6 is an illustration of cross-well electromagnetic tomography measurements between two wells;

Figure 7 is a schematic illustration of enhanced water flood imaging via co-injection of contrast agents; and

Figure 8 is a schematic illustration of the use of contrast agents to illuminate fractures in hydraulic fracturing applications.

DETAILED DESCRIPTION

Compositions and methods are disclosed for use in geological exploration, mining and recovery of natural resources. The compositions and methods disclosed herein can provide for the identification of subterranean features during geological exploration. The compositions and methods can, for example and without limitation, be used for the exploration, mining and recovery of oil and natural gas. The compositions and methods can be used to locate and define reservoirs of oil and natural gas and estimate the quantity of oil and natural gas capable of being recovered. The disclosed compositions and methods can be used to monitor recovery and safety during the extraction of oil and natural gas.

Traditional methods of oil recovery can be inefficient. For example, after the primary recovery of oil from a reservoir, about 30-70% residual oil in place (ROIP) remains in the reservoir in the form of ganglions, which are oil blobs that are generally a few pore-lengths long (in the direction of the flow) and about a pore wide. In some embodiments, the disclosed compositions and methods can be used to locate and estimate ROIP in reservoirs, which can then be recovered to increase the efficiency of oil recovery.

Contrast agents or compositions are disclosed herein that can be used in geological exploration, mining and recovery. The contrast agents can be used to locate and define reservoirs of oil and natural gas and estimate the quantity of oil and natural gas capable of being recovered. The contrast agents can allow for the monitoring of the recovery of oil and natural gas, both to improve efficiency and ensure safety. The contrast agents can allow for the identification and definition of subterranean features.

Contrast agents and methods can selectively enhance the dielectric effects of ganglions of oil, for example, by decorating or otherwise suitably exposing the oil-water interfaces with the contrast agent. In some embodiments, a dilute suspension of the contrast agent can be injected into an oil or natural gas well such that the contrast agents can migrate to and decorate the oil or natural gas deposit. These deposits can then be illuminated by deep reading electromagnetic tools as disclosed herein.

By way of example and not limitation, the contrast agents provided herein can comprise low-frequency dielectric permittivity contrast agents. In some embodiments, the disclosed contrast agents can comprise any nanopolymorph or any nanomaterial, such as but not limited to, nanotubes, nanosheets, and nanoparticles. In some embodiments, the disclosed contrast agents can be titania nanotubes (TiNT) or TiNT-based contrast agents. Among other things, Na-titania nanotubes can show significant dielectric contrast.

Methods are disclosed herein for identifying subterranean features during geological exploration, mining and recovery. In some embodiments, the disclosed methods can comprise providing a geological exploration site, such as for example an oil well, natural gas well, or mine shaft; providing a contrast agent; providing an electromagnetic tool; administering a contrast agent into the exploration site; allowing the contrast agent to migrate to a subterranean feature in the exploration site; and illuminating the subterranean feature using the electromagnetic tool.

In some embodiments, the presently disclosed methods and compositions can be employed alongside existing technologies, and in some embodiments enhance the effectiveness of existing technologies currently used in the oil and gas industries. Such existing technologies can include, for example, existing deep electromagnetic tools. The advantages and benefits imparted by the presently disclosed methods and compositions are based on a number of considerations. For example, deep electromagnetic probing tools penetrate deeper and farther away from the well-bore at lower measurement frequencies. Additionally, dielectric permittivity is substantially enhanced at lower frequencies when immobile charges are balanced by mobile counter-ions such as in clay systems. And contrast agents, such as TiNTs with robust clay-like structures having natural affinity to oil-water interfaces, can be injected into a well or other subterranean structure as a suspension thereby allowing the contrast agents to migrate to the oil-water interface and illuminate the oil phase with substantially enhanced dielectric permittivity at lower frequencies.

I. Definitions

While the following terms are believed to be well understood by one of ordinary skill in the art, the following definitions are set forth to facilitate explanation of the presently disclosed subject matter.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which the presently disclosed subject matter belongs. Although any methods, devices, and materials similar or equivalent to those described herein can be used in the practice or testing of the presently disclosed subject matter, representative methods, devices, and materials are now described.

Following long-standing patent law convention, the terms “a” and “an” mean “one or more” when used in this application, including the claims.

Unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about”. Accordingly, unless indicated to the contrary, the numerical parameters set forth in this specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the presently disclosed subject matter.

As used herein, the term “about,” when referring to a value or to an amount of mass, weight, time, volume, concentration or percentage is meant to encompass variations of in some embodiments ±20%, in some embodiments ±10%, in some embodiments ±5%, in some embodiments ±1%, in some embodiments ±0.5%, and in some embodiments ±0.1% from the specified amount, as such variations are appropriate to perform the disclosed method.

As used herein, “significance” or “significant” relates to a statistical analysis of the probability that there is a non-random association between two or more entities. To determine whether or not a relationship is “significant” or has “significance”, statistical manipulations of the data can be performed to calculate a probability, expressed as a “p value”. Those p values that fall below a user-defined cutoff point are regarded as significant.

In some embodiments, a p value less than or equal to 0.05, in some embodiments less than 0.01, in some embodiments less than 0.005, and in some embodiments less than 0.001, are regarded as significant. Accordingly, a p value greater than or equal to 0.05 is considered not significant.

As used herein, the term "and/or" when used in the context of a listing of entities, refers to the entities being present singly or in combination. Thus, for example, the phrase "A, B, C, and/or D" includes A, B, C, and D individually, but also includes any and all combinations and subcombinations of A, B, C, and D. The term "comprising", which is synonymous with "including", "containing", or "characterized by" is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. "Comprising" is a term of art used in claim language which means that the named elements are present, but other elements can be added and still form a construct or method within the scope of the claim.

As used herein, the phrase "consisting of" excludes any element, step, or ingredient not specified in the claim. When the phrase "consists of" appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

As used herein, the phrase "consisting essentially of" limits the scope of a claim to the specified materials or steps, plus those that do not materially affect the basic and novel characteristic(s) of the claimed subject matter.

With respect to the terms "comprising", "consisting of", and "consisting essentially of", where one of these three terms is used herein, the presently disclosed and claimed subject matter can include the use of either of the other two terms.

As used herein, the term "decorate", when used in conjunction with contrast agents, such as TiNT, refers to the collection of contrast agents around, near, in proximity to, or within a subterranean feature or oil ganglion. In some embodiments a subterranean feature or oil ganglion that is "decorated" by contrast agents can be coated with or otherwise substantially surrounded by a layer of contrast agent. A subterranean feature or oil ganglion "decorated" by contrast agents can be illuminated by deep reading electromagnetic tools based on the enhanced dielectric permittivity imparted by the contrast agents. In some embodiments, to sufficiently "decorate" an oil ganglion such that it is visible by electromagnetic tomography the coating of contrast agent need only be about 2 nanometers thick to about 20 nanometers thick.

II. Contrast Agents

Contrast agents or compositions are disclosed herein that can be used in geological exploration, mining and recovery, or in other applications as would be appreciated by one of ordinary skill in the art. In some embodiments, the contrast agents can be used to locate and define reservoirs of oil and/or natural gas. In some embodiments, the contrast agents can estimate the quantity of oil and/or natural gas capable of being recovered. In some embodiments, the contrast agents can allow for the monitoring of the recovery of oil and/or natural gas, to improve efficiency and/or ensure safety.

The contrast agents, and methods of using the same, can selectively enhance the dielectric effect of ganglions of oil or subterranean features, for example, by decorating or otherwise suitably exposing the oil-water interfaces with the contrast agent. In some embodiments, a dilute suspension of the contrast agent can be injected into an oil or natural gas well such that the contrast agents can migrate to and decorate an oil or natural gas deposit, or other subterranean feature. These deposits or subterranean features can then be illuminated by deep reading electromagnetic tools as discussed further herein.

By way of example and not limitation, the contrast agents provided herein can comprise low-frequency dielectric permittivity contrast agents. In some embodiments, a low-frequency dielectric permittivity can comprise a frequency range of 10kHz and below, such as for example, 1kHz, 2kHz, 3kHz, 4kHz, 5kHz, 6kHz, 7kHz, 8kHz, 9kHz or 10kHz. In some embodiments, the disclosed contrast agents can comprise any nanopolymorph or any nanomaterial, such as but not limited to, nanotubes, nanosheets, nanoparticles, and combinations thereof. In some embodiments, the disclosed contrast agents can be TiNT-based contrast agents. Among other things, Na-TiNTs can show significant dielectric contrast and are therefore suitable contrast agents for the presently disclosed subject matter. As would be appreciated by one of ordinary skill in the art, any agent that has a low-frequency dielectric permittivity can in some embodiments be a suitable agent in accordance with the instant disclosure.

Contrast agents disclosed herein, such as TiNT or nano-clays, are stable and require no functionalization by organic molecules. In some embodiments, when the disclosed contrast agents are present in briny suspensions, they can be surrounded by mobile counter-ions native to the brine that form a double layer around the contrast agents. The mobile counter-ions in the double layer can move under the influence of an electromagnetic field giving rise to a large dielectric enhancement. In bare contrast agents, devoid of Na^+ ions, or dry contrast agents, this enhancement will be dormant as no counter-ions are available or not mobile, respectively.

Suspensions of contrast agents can be provided in some embodiments. The contrast agents disclosed herein can form a stable suspension in solutions, such as for example water or a briny solution. Fresh water or sea water (salt water) can be acceptable solutions in some embodiments. When suspended in water, for example, the contrast agents can remain stable under very wide pH and salinity ranges that are suitable for naturally occurring formation conditions. The concentration of the contrast agent in a solution can be as low as a few volume percent, such as for example 1%, 2%, 3%, 4%, 5%, 10%, 15%, 20%, 30%, 40%, 50% or more.

The unique structures of TiNTs have properties in common with clays. For example, TiNTs comprise a substantial amount of exchangeable Na^+. As disclosed herein, in some embodiments TiNTs can show considerable enhancement of permittivity when saline water penetrates them by forming double layers. As disclosed herein, contrast agents such as TiNTs have natural affinity toward water-oil interfaces and can therefore be used to illuminate oil ganglions by enhancing their dielectric permittivity. When a thin layer of contrast agent coats an oil ganglion or other subterranean feature, the effective property of the ganglion or subterranean feature towards an electromagnetic wave will change. An effective medium calculation shows that when a large contrast of properties is present, a very small volume fraction of contrast agent will suffice to illuminate the reservoir—*i.e.*, ganglions or subterranean features will show up in electromagnetic measurements. The intrinsic dielectric enhancement in these systems has not previously been explored and offers a tremendous opportunity for use in the use in geological exploration, mining and recovery, and particularly in identifying and extracting bypassed oil.

Using the dielectric theory, the complex dielectric constant of materials can be expressed by complex (relative) permitivities:

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = \varepsilon'(\omega) + i\,\sigma(\omega)/(\varepsilon_0\,\omega) \qquad \text{(Equation 1)}$$

where ε' is the real permittivity, ε" is the imaginary permittivity, ε_0 is the permittivity of a vacuum, and σ(ω) is the conductivity.

The dielectric (relative) permittivity of a TiNT suspension, such as for example TiNTs in an electrolyte solution, can be 5,000 or more (in unit of the vacuum permittivity, which is 8.854×10^{-12} $F{\cdot}m^{-1}$), especially at low frequencies. This is markedly higher than the dielectric permittivity of dry TiNTs, such as TiNTs not in solution, which is about 5 (in unit of the vacuum permittivity, which is 8.854×10^{-12} $F{\cdot}m^{-1}$). The dielectric permittivity of a TiNT suspension is also markedly higher that the electrolyte suspension alone, which has a dielectric permittivity of about 80 (in unit of the vacuum permittivity, which is 8.854×10^{-12} $F{\cdot}m^{-1}$). Standard Maxwell-Wagner/Maxwell-Garnett analysis for a two-phase material is unable to explain such results. Instead, without being bound by any particular theory of operation, it is believed that the charged double layers surrounding the particles are responsible for this enhancement in dielectric permittivity observed in a Na-TiNT suspension.

Such a dielectric effect has been observed on induction logs at low frequencies in some peculiar rock formations. Without limitation as to any particular theory, it is believed that the reason for the large dielectric effect lies in the nature of the particular shaly sand, such as clay bearing sands, in the formation. Such formations can have abnormally high ε' between 10,000 and 30,000 even at low frequencies (induction tool, tens of kHz). Such high dielectric permittivities at low frequencies can originate from the microstructure of the clay, which can give rise to the double layer effect due to counter-ions (Na^+ or Ca^{++}) that are mobile in the presence of water. Such double layers are illustrated in Figure 1.

Figure 1 is a diagram showing clay or titanium dioxide (TiO_2) **20** double-layer polarization **24** at the particle level. Positive counter-ions **22** lead to low polarization. Presence of water mobilizes the counter-ions leading to enhanced dielectric contrast. The polarization of exchangeable Ca^{++} and Na^+ counter-ions **22** outside the lattice in the presence of water gives rise to interfacial polarization as illustrated in Figure 1.

Figure 2A illustrates electric double layers formed around contrast agents **28**, such as TiNT, with bound negative charges **24** balanced by mobile positive counter-ions **22**. Negative charges **24** create a double-layer polarization at the particle level.

Figure 2B illustrates oil ganglions **26** decorated with contrast agents **28**, such as TiNTs, in contact with formation water **30**. Formation water **30** comprises water naturally found in a subterrain reservoir. The counter-ions in formation water **30** polarize in the presence of an electromagnetic wave giving rise to significant dielectric permittivity.

III. Dielectric Permittivity Effect

Titania is a clay-like material with an electrochemical double layer and can possess very large dielectric constants of $\varepsilon(\omega) \approx 10^6$ in the presence of water. In comparison, water alone has a value of 80 and most oils fall below 2. This is the basis for the use of dielectric materials as contrast agents for enhanced contrast in subterranean applications, such as locating bypassed oil and other geologic and mining applications.

The propagation of electromagnetic wave $E(x,t) = E_0 e^{i(kx-\omega t}$ is determined by $k = \alpha(\omega) + i\beta(\omega)$ where $\alpha(\omega)$ gives a phase shift, whereas

$\beta(\omega)$ gives rise to attenuation. Dielectric logging tools measure $\alpha(\omega)$ and $\beta(\omega)$. It can be shown based on the theory of electromagnetism that:

$$k^2 = i\omega\mu(\sigma - i\omega\varepsilon_0\varepsilon') \quad \text{(Equation 2)}$$

where σ is the conductivity and μ is the permeability. Equation 2 shows clearly that the conductivity effect dominates over the dielectric effect at low frequencies because of the ω dependence. However, this is not the case with the enhanced dielectric constant of contrast agents as disclosed herein, such as for example TiNT in suspension.

Figure 3 is a graphical representation comparing the dielectric enhancement of Bentonite clay and TiNT as a function of frequency. Bentonite is tested at 5 wt% (long dashed line) and 10 wt% (short dashed line), while TiNT was tested at 10 wt% (dotted line) and 15 wt% (dashed and dotted line). NaCl (solid line) solution was used as a control. The dielectric properties of Bentonite clay are established. As expected, Bentonite clay has a significantly higher dielectric enhancement than the control NaCl. As illustrated in Figure 3, TiNT, which have similar structural characteristics as Bentonite clay, also achieve enhanced dielectric permittivity at lower frequencies as compared to NaCl.

IV. Contrast Agents with Sensing Membranes

Contrast agents as disclosed herein, such as TiNTs, in briny suspensions can be surrounded by mobile counter-ions native to the brine that form a double layer around the contrast agents. The mobile counter-ions in the double layer can move under the influence of an electromagnetic field giving rise to a large dielectric enhancement. However, in bare contrast agents, devoid of Na^+ ions, or dry contrast agents, this enhancement will be dormant as no counter-ions are available or not mobile, respectively. When such contrast agents are encapsulated within a membrane they are rendered dielectrically inactive as well since no double layer can form around the contrast agent. In some embodiments, the membrane can be designed to be sensitive to an environmental stimulus or a predetermined condition. Such an encapsulation, referred to herein as a sensing membrane, can for example be time sensitive. That is, the sensing membrane can be sensitive to a predetermined period of time that has elapsed since immersion into a reservoir, for example. A time-sensitive membrane can provide for a passive sensing mechanism for geolocation, e.g., a smart tracer with the ability to be detected by an electromagnetic transmitter and receiver *in situ*.

In some embodiments, a sensing membrane can be sensitive to one or more specific reservoir conditions, such as temperature, pH, salinity, pressure, or any other predetermined threshold value of any environmental stimuli or condition. When exceeding a given threshold or encountering such a stimulus, the sensing membrane can become permeable or otherwise deteriorate structurally such that briny reservoir fluid is admitted into the membrane and comes into contact with the contrast agent. Upon admission of briny fluid and/or interaction with briny fluid, the contrast agent is provided with the necessary counter-ions to form a double layer. Thereafter, when interrogated with electromagnetic waves, the contrast agent that is now surrounded by counter-ions to form a double layer can exhibit a large dielectric enhancement and thereby act as beacons signaling that the contrast agents encountered the threshold value in geological conditions preprogrammed into the sensing membrane.

Figure 4 is a schematic representation of contrast agents encapsulated with a sensing membrane, also referred to as switchable dielectric induced polarization sensors. In Figure 4, contrast agent or agents **62** are surrounded by or encapsulated by a membrane **92** that is sensitive to an environmental stimulus or multiple environmental stimuli. Contrast agents **62** encapsulated by membrane **92** are activated upon encountering an environmental stimulus **94** (e.g., temperature, pressure, etc.). Upon encountering environmental stimulus **94**, membrane **92** becomes permeable or otherwise deteriorates. Alternatively, or in addition, membrane **92** can be designed to decay at a predetermined time interval or within a set time period. Once membrane **92** becomes permeable, briny reservoir fluid can be admitted through the membrane such that it can come into contact with the contrast agent **62**. Thereafter, contrast agent **62** can be detected using probing tools due to its large dielectric enhancement.

V. Synthesis of Titania Nanotube Contrast Agents

Titania nanotube is a newer form of titania. In some embodiments, the starting material of synthesis can be many different sources of commercially available titania powders, such as, for example, anatase nanocrystals and P25 consisting of anatase and rutile mixture. In some embodiments, such titania powder can be immersed in 10 M NaOH and heated in a Teflon®-lined autoclave at about 130°C for about 72 hours, although the temperature can range from about 110°C to about 150°C, and the time can be 12 hours or more. This hydrothermal process converts starting materials into TiNTs. To remove the intercalated Na^+ ions, the material produced can be washed with H_2O, or with diluted HCl then H_2O to reduce the pH value. In some embodiments, the yield of TiNTs can be over 90% of the total titania material. This process of synthesizing TiNTs can be economical and can be scalable to an industrial level. Figure 5A is a transmission electron microscopy (TEM) image of as-synthesized TiNT. In Figure 5A, the multilayered tubular structure are clearly visible. Using TEM imaging, the inner diameters of the TiNT in Figure 5A are about 5 nm to about 6 nm, the outer diameters about 10 nm to about 12 nm, and interlayer spacings about 0.87 nm. Figure 5B is a scanning electron microscopy (SEM) image of TiNTs showing the high yield of the synthesis process.

VI. Identifying subterranean features using contrast agents

Methods are disclosed herein for identifying subterranean feature(s) during geological exploration, mining and the recovery of natural resources. In some embodiments, the disclosed methods can comprise providing a geological exploration site, such as for example an oil well, natural gas well, or mine shaft. The methods can employ a contrast agent that has significant dielectric contrast. In some embodiments, an electromagnetic tool or tools can be used in the disclosed methods to detect the contrast agent and identify a subterranean feature. In some embodiments, such methods can include the following steps: administering a contrast agent into the exploration site; allowing the contrast agent to migrate to a subterranean feature in the exploration site; and illuminating or visualizing the subterranean feature using an electromagnetic tool.

The contrast agent or agents employed in the disclosed methods for identifying a subterranean feature can comprise any contrast agent or combinations of contrast agents as disclosed herein. By way of example and not limitation, the contrast agent can comprise a nanopolymorph material having a low-frequency dielectric permittivity. Such a nanopolymorph material can comprise a nanotube, a nanosheet and/or a nanoparticle. More particularly, TiNTs, as discussed in further detail herein, can be used as the contrast agent for identifying or illuminating a subterranean feature.

Such contrast agents are effective in methods of identifying subterranean features due to their high dielectric constant, which provides for high dielectric permittivity. Such properties allow for the detection of contrast agents within a subterranean feature thereby allowing for the visualization of the subterranean feature using an appropriate electromagnetic tool. As discussed further herein, the contrast agents can have a dielectric permittivity that is greater than about 5,000 to about 10 million in unit of vacuum permittivity.

As discussed herein, the contrast agents can further comprise a membrane or coating encapsulating the contrast agent, wherein the membrane can become permeable or deteriorate upon encountering an environmental stimulus. The environmental stimulus to which the membrane or coating is sensitive can be purposefully selected and predetermined based on the desired application. For example, a membrane can sense and become permeable in response to a desired pH, temperature, pressure, salinity, time period, or combinations thereof.

In some embodiments, a contrast agent can be administered to an exploration site where it is desirable to identify and characterize a subterranean feature by mixing the contrast agent in a solution and depositing the solution in the exploration site. That is, a solution containing the contrast agent can be deposited or pumped into a bore hole, well, or mine shaft. The contrast agent solution can then permeate the subterranean geological features surrounding the exploration site. Once a sufficient time has passed for the contrast agent solution to migrate to the subterranean feature or area to be explored, an electromagnetic tool can be used to visualize the subterrain. In some embodiments, a sufficient time for the contrast agent solution to migrate to the subterranean feature or area to be explored can range from a few days to several months. More particularly, a sufficient migration time can be about 1 day, 2 days, 3 days, 4 days, 5 days, 6 days, 7 days, 8 days, 9 days, 10 days or more, or about 1 month, 2 months, 3 months, 4 months, 5 months or more.

In some embodiments, the solution can comprise an electrolyte solution. In some embodiments, an electrolyte solution can comprise NaCl. The contrast agents disclosed herein can form a stable suspension in solutions, such as for example water or a briny solution. Fresh water or sea water (salt water) can be acceptable solutions in some embodiments. When suspended in water, for example, the contrast agents can remain stable under very wide pH and salinity ranges that are suitable for naturally occurring formation conditions. The concentration of the contrast agent in a solution can be as low as a few volume percent, such as for example 1%, 2%, 3%, 4%, 5%, 10%, 15%, 20%, 30%, 40%, 50% or more.

Once a contrast agent is administered to an exploration site, and in some embodiments after the contrast agent and/or the solution containing the contrast agent has migrated to a subterranean feature in the exploration site, an electromagnetic tool can be used to detect the contrast agents within a subterranean feature. Because of the dielectric contrast of the contrast agents the electromagnetic tool will allow for the visualization of any subterranean feature penetrated and/or surrounded by the contrast agent solution.

The electromagnetic tools used in the disclosed methods of visualizing subterranean features can in some embodiments include existing technologies currently used in the oil and gas industries. Such existing technology can include, for example, existing deep electromagnetic tools. For instance, cross-well electromagnetic tomography can be used in conjunction with the disclosed contrast agents to visualize subterranean features. Cross-well electromagnetic tomography, when operated at low frequencies, has a penetration range of up to about 1 kilometer (3,280 feet) compared to logging while drilling (LWD) systems, which can only probe up to about 20 feet.

Figure 6 is an illustration of cross-well electromagnetic tomography used in two separate wells. For example, cross-well electromagnetic tomography can be used to take measurements between two wells (first well **32** and second well **34**) separated by a given distance **r** up to 1,000 meters. Cross-well electromagnetic tomography can operate at the frequency range of about 10 Hz to about 100 Hz for cased wells and up to about 1 kHz for open wells. A first well **32** can comprise a transmitter **36** and receiver **38** for transmitting and receiving an electromagnetic signal **42**, respectively. Sensitivity to a subterrainean formation, such as bypassed oil ganglions, increases with conductivity and dielectric constant. As such, the use of a contrast agent in conjunction with cross-well electromagnetic tomography as discussed herein can enhance sensitivity to formation detection.

VII. Illuminating Bypassed Oil Using Titania Nanotubes

Traditional methods of oil recovery can be inefficient. For example, after the primary recovery of oil from a reservoir, about 30-70% residual oil in place (ROIP) remains in the reservoir in the form of ganglions, which are oil blobs that are generally a few pore-lengths long (in the direction of the flow) and about a pore wide. In some embodiments, the disclosed compositions and methods can be used to locate and estimate ROIP in reservoirs, which can then be recovered to increase the efficiency of oil recovery.

In some embodiments, methods are provided for using the disclosed contrast agents to make ganglions of bypassed oil visible towards deep penetrating electromagnetic probing tools. For example, in some embodiments such a method can comprise providing a contrast agent, providing an electromagnetic tool, administering a contrast agent into an oil well, allowing the contrast agent to migrate to a ganglion of bypassed oil in the oil well, and illuminating the ganglion of bypassed oil using the electromagnetic tool. Such methods can in some embodiments employ contrast agents that can have a significant dielectric contrast. In some embodiments, TiNT, such as Na-titania oxide nanotubes, as well as nano-clays, can show significant dielectric contrast and can therefore serve as contrast agents. The disclosed methods can selectively enhance the dielectric effects of ganglions by decorating the oil-water interfaces with contrast agents, which are stable and, in embodiments, require no functionalization by organic molecules. In some embodiments, a dilute suspension of the contrast agent can be injected into a well near a ganglion of bypassed oil so that the contrast agent can migrate through the subterrain where the oil ganglia is located. These ganglia can then be illuminated by deep reading electromagnetic tools due to the dielectric activity of the contrast agents surrounding the oil ganglia.

In some embodiments, the disclosed compositions and methods can provide for illuminating bypassed oil using TiNT. The unique structures of TiNT share some structural qualities with clays. Titania nanotubes comprise a substantial amount of exchangeable Na^+. As disclosed herein, in some embodiments, TiNT can show considerable enhancement of permittivity when saline water penetrates them by forming double layers. As disclosed herein, TiNT have a natural affinity toward water-oil interfaces and can therefore be used to illuminate oil ganglions by enhancing their dielectric permittivity as illustrated in Figure 2B.

When a thin layer of contrast agent coats an oil ganglion, the effective property of ganglion towards an electromagnetic wave will change. An effective medium calculation shows that when a large contrast of properties is present, a very small volume fraction of contrast agent will suffice to illuminate the reservoir. That is, oil ganglions will show up in electromagnetic measurements when surrounded by contrast agents. For example, for an oil ganglion of about 100 micron, which is about the normal size of the capillary number encountered in the usual recovery of hydrocarbons from a subterranean structure, a coating by a contrast agent such TiNT of a thickness of about 6 nanometers will suffice if the dielectric permittivity contrast of the contrast agent differs by about a factor of 1,000 or more from that of oil, water, or rock. For tighter pores and thinner ganglions, even less contrast will suffice. Thus, to sufficiently decorate an oil ganglion such that it is visible by electromagnetic tomography the coating of contrast agent need only be about 2 nanometers thick to about 20 nanometers thick.

The disclosed methods can selectively enhance the dielectric effects of oil ganglions by decorating the oil-water interfaces with contrast agents, such as TiNT or nano-clays, which are stable and require no functionalization by organic molecules. In some embodiments, a dilute suspension of the contrast agent, such as TiNT (with suitable counter-ions), can be injected near a bypassed oil pool. The contrast agent, such as TiNT, can migrate to decorate the oil ganglia. These ganglia can then be illuminated by deep reading electromagnetic tools.

The dielectric enhancement of existing electromagnetic tomography systems using the disclosed contrast agents has not previously been explored and offers a tremendous opportunity for use in the use in geological exploration, mining and recovery, and particularly in identifying and extracting bypassed oil.

As discussed herein, the electromagnetic tools used in the disclosed methods of visualizing oil ganglia can in some embodiments include existing technologies currently used in the oil and gas industries. Such existing technology can include, for example, existing deep electromagnetic tools. For instance, cross-well electromagnetic tomography can be used in conjunction with the disclosed contrast agents to visualize subterranean features. Cross-well electromagnetic tomography, when operated at low frequencies, has a penetration range of up to about 1 kilometer (3,280 feet) compared to logging while drilling (LWD) systems which can only probe up to about 20 feet.

Figure 6 is an illustration of an example of cross-well electromagnetic tomography used in two separate wells. For example, cross-well electromagnetic tomography can be used to take measurements between two wells (first well **32** and second well **34**) separated by a given distance **r** up to 1,000 meters. Cross-well electromagnetic tomography can operate at the frequency range of about 10 Hz to about 100 Hz for cased wells and up to about 1 kHz for open wells. A first well **32** can comprise a transmitter **36** and receiver **38** for transmitting and receiving an electromagnetic signal **42**, respectively. Sensitivity to a subterrainean formation, such as bypassed oil ganglions, increases with conductivity and dielectric constant. As such, the use of a contrast agent in conjunction with cross-well electromagnetic tomography as discussed herein can enhance sensitivity of the cross-well electromagnetic tomography equipment for detection of features in the subterrainean formation **44**.

Figure 7 is a schematic illustration of an example of enhanced water flood imaging via co-injection of contrast agents, such as those disclosed herein. Similar to the cross-well electromagnetic tomography illustrated in Figure 6, electromagnetic tomography measurements can be taken between two wells (first well **52** and second well **54**). As illustrated in Figure 6, first well **52** can act as an injection well, and second well **54** can act as a production well. Container **70** can supply the contrast agent **62**, and production equipment **72** can recover the contrast agent **62** as well as gas or oil produced by second well **54**. Contrast agent **62** can be injected as part of a solution into first well **52** and allowed to flow through the subterrain and interact with any subterranean feature. The first well **52** can comprise a transmitter **56** for transmitting an electromagnetic signal **64**, while the second well **54** can comprise a receiver **58** for receiving an electromagnetic signal **64**. Any subterranean feature decorated or surrounded by the contrast agent **62** can be detected based on the enhanced dielectric permittivity imparted by the contrast agent **62**. Sensitivity to a subterranean formation increases with conductivity and dielectric constant. Therefore, the use of a contrast agent **62** in conjunction with cross-well electromagnetic tomography as discussed herein can enhance sensitivity of the cross-well electromagnetic tomography equipment to formation detection of features in the subterrainean formation.

VIII. Use of Contrast Agents in Hydraulic Fracturing

In some embodiments, methods are provided herein for using the disclosed contrast agents in natural gas extraction and exploration. In some embodiments, the disclosed contrast agents and methods of using the same can be employed in natural gas extraction techniques, such as induced hydraulic fracturing, also known as fracking or hydrofracking. Presently available techniques employed in hydraulic fracturing are not adequate to determine the size and orientation of fractures in the subterrain. Determining the size and orientation of a fracture is beneficial to determining the drainage of a reservoir, and for the safe and effective extraction of natural gas.

Using the disclosed contrast agents along with electromagnetic probing tools can allow for the visualization and delineation of the size, orientation, and other parameters needed for safe and/or effective hydraulic fracturing, such as for example illuminating the fracture and tracking the flow of hydraulic fluids. In some embodiments, a fracture can be filled with a suspension containing the presently disclosed contrast agents and then visualized using probing tools. Figure 8 is a schematic illustration of the use of contrast agents to illuminate fractures in hydraulic fracturing applications. Figure 8 is a top-down cross-sectional view of a bore hole **82** and fracture **84** in the subterrain. Bore hole **82** can be used to provide access to fracture **84** in the subterrain so that a suspension of contrast agent **62** can be pumped into fracture **84**. The suspension of contrast agent **62** can infiltrate fracture **84** such that contrast agent **62** outlines the contours of fracture **84**. As with the oil well applications discussed herein, electromagnetic probing tools and electromagnetic tomography methodologies can then be used to visualize the contours and properties of fracture **84**.

CLAIMS

What is claimed is:

1. A method of identifying a subterranean feature during geological exploration, comprising:

administering a contrast agent into a geological exploration site;

allowing the contrast agent to migrate to a subterranean feature in the geological exploration site; and

illuminating the subterranean feature using an electromagnetic tool suitable for sensing a presence of the contrast agent that has migrated to the subterranean feature.

2. The method of claim 1, wherein the contrast agent comprises a nanopolymorph material having a low-frequency dielectric permittivity.

3. The method of claim 2, wherein the nanopolymorph material is selected from the group consisting of a nanotube, a nanosheet, and a nanoparticle.

4. The method of claim 2, wherein the nanopolymorph material is a TiNT.

5. The method of claim 2, wherein a dielectric permittivity of the contrast agent is greater than about 5,000 (F/m).

6. The method of claim 2, further comprising a membrane encapsulating the contrast agent.

7. The method of claim 6, wherein the membrane is configured to be permeable upon encountering a stimulus selected from the group consisting of pH, temperature, pressure, salinity, and combinations thereof.

8. The method of claim 6, wherein the membrane is configured to be permeable after a predetermined period of time has elapsed.

9. The method of claim 2, wherein the contrast agent is stable at a temperature up to about 350°C and a pH ranging from about 1 to about 12.

10. The method of claim 2, further comprising mixing the contrast agent into a solution prior to administering the contrast agent into the geological exploration site.

11. A contrast agent suitable for use in geological applications, the contrast agent comprising a nanopolymorph material having a low-frequency dielectric permittivity.

12. The contrast agent of claim 11, wherein the nanopolymorph material is selected from the group consisting of a nanotube, a nanosheet, and a nanoparticle.

13. The contrast agent of claim 11, wherein the nanopolymorph material is a titanium nanotube.

14. The contrast agent of claim 11, wherein the dielectric permittivity of the contrast agent is greater than about 5,000 Farads/meter (F/m).

15. The contrast agent of claim 11, further comprising a membrane encapsulating the contrast agent.

16. The contrast agent of claim 15, wherein the membrane is configured to be permeable upon encountering a stimulus selected from the group consisting of pH, temperature, pressure, salinity, and combinations thereof.

17. The contrast agent of claim 15, wherein the membrane is configured to be permeable after a predetermined period of time has elapsed.

18. The contrast agent of claim 11, wherein the contrast agent is stable at a temperature up to about 350°C and a pH ranging from about 1 to about 12.

19. The contrast agent of claim 11, wherein the contrast agent can be mixed into a solution.

20. The contrast agent of claim 11, wherein the contrast agent is configured to have an affinity toward the interface between water and oil.

21. A method of identifying a ganglion of bypassed oil in a geological formation, comprising:

administering a contrast agent into the geological formation through a well bore, wherein the contrast agent migrates to the ganglion of bypassed oil in the geological formation; and

illuminating the ganglion of bypassed oil using an electromagnetic tool suitable for sensing a presence of the contrast agent that has migrated to the ganglion of bypassed oil.

22. The method of claim 21, wherein the contrast agent comprises a nanopolymorph material having a low-frequency dielectric permittivity.

23. The method of claim 22, wherein the nanopolymorph material is selected from the group consisting of a nanotube, a nanosheet, and a nanoparticle.

24. The method of claim 22, wherein the nanopolymorph material is a titania nanotube.

25. The method of claim 22, wherein a dielectric permittivity of the contrast agent is greater than about 5,000 (F/m).

26. The method of claim 21, further comprising a membrane encapsulating the contrast agent.

27. The method of claim 26, wherein the membrane is configured to be permeable upon encountering a stimulus selected from the group consisting of pH, temperature, pressure, salinity, and combinations thereof.

28. The method of claim 26, wherein the membrane is configured to be permeable after a predetermined period of time has elapsed.

29. The method of claim 21, wherein the contrast agent is stable at a temperature up to about 350°C and a pH ranging from about 1 to about 12.

30. The method of claim 21, further comprising mixing the contrast agent into a solution prior to administering the contrast agent into the geological formation.

31. The method of claim 21, wherein the contrast agent wherein the contrast agent is configured to have an affinity toward the interface between water and oil.

32. A method of illuminating a subterrain fracture, comprising:

administering a contrast agent into the subterrain fracture through a bore hole; and

illuminating the subterrain fracture using an electromagnetic tool suitable for sensing a presence of the contrast agent.

33. The method of claim 32, wherein the contrast agent comprises a nanopolymorph material having a low-frequency dielectric permittivity.

34. The method of claim 33, wherein the nanopolymorph material is selected from the group consisting of a nanotube, a nanosheet, and a nanoparticle.

35. The method of claim 33, wherein the nanopolymorph material is a titania nanotube.

36. The method of claim 35, wherein a dielectric permittivity of the contrast agent is greater than about 5,000 (F/m).

37. The method of claim 32, further comprising a membrane encapsulating the contrast agent.

38. The method of claim 37, wherein the membrane is configured to be permeable upon encountering a stimulus selected from the group consisting of pH, temperature, pressure, salinity, and combinations thereof.

39. The method of claim 37, wherein the membrane is configured to be permeable after a predetermined period of time has elapsed.

40. The method of claim 32, wherein the contrast agent is stable at a temperature up to about 350°C and a pH ranging from about 1 to about 12.

41. The method of claim 32, further comprising mixing the contrast agent into a solution prior to administering the contrast agent into the subterrain fracture.

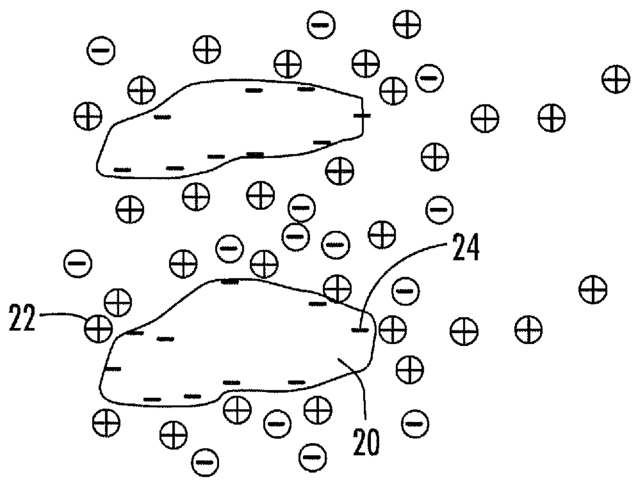


FIG. 1

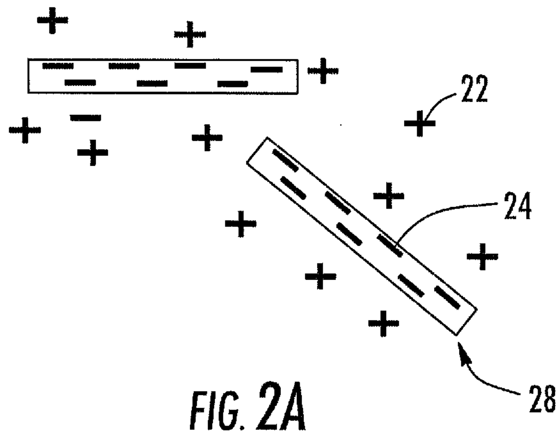


FIG. 2A

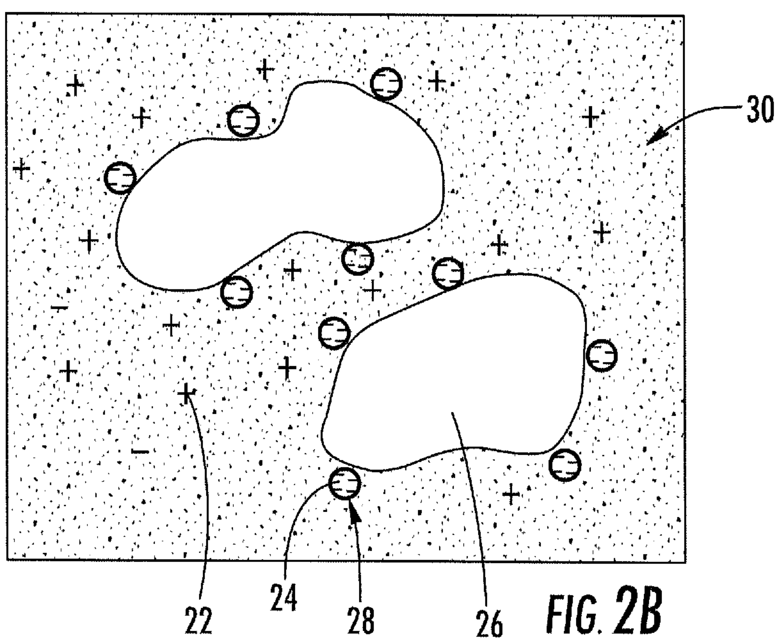
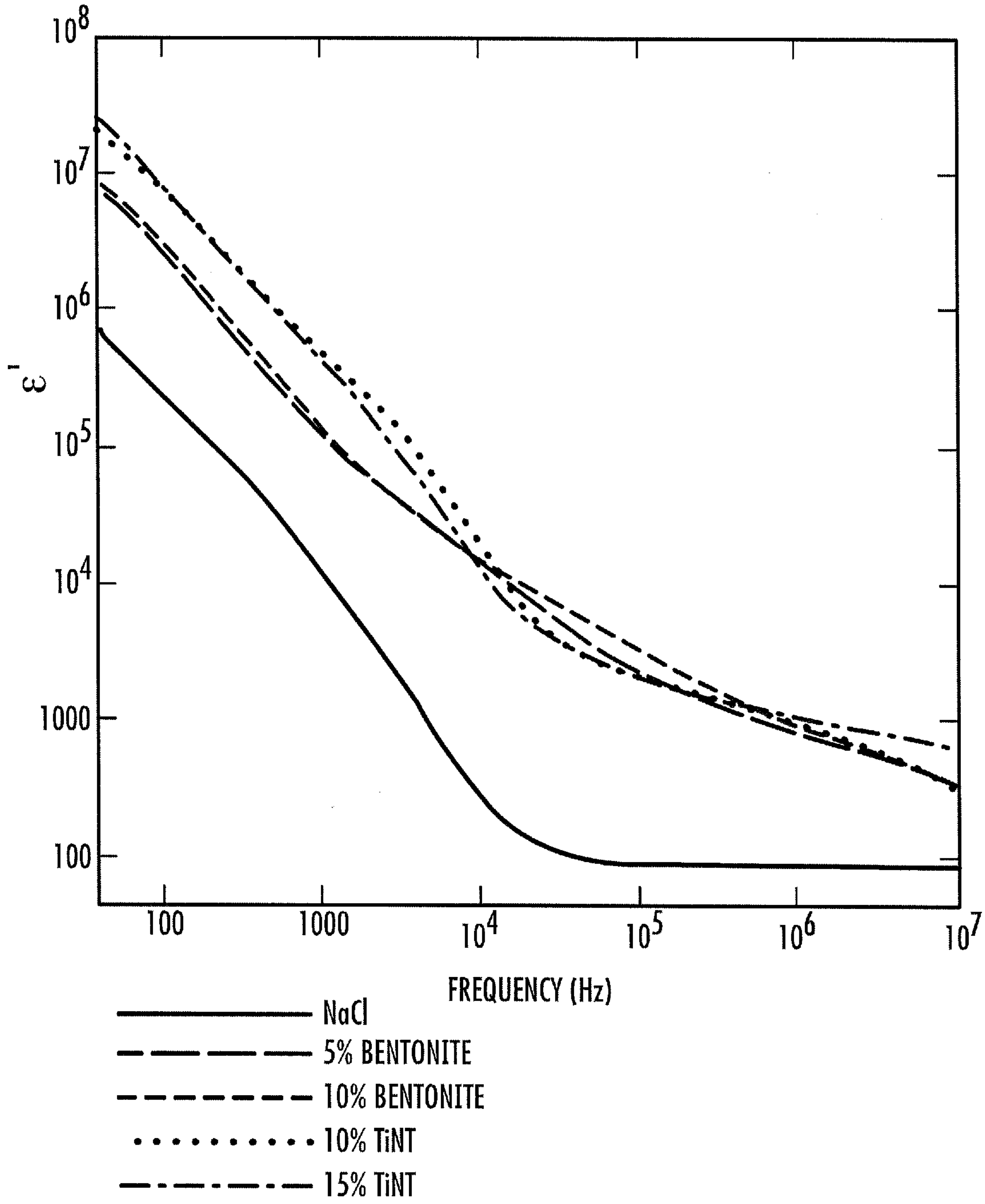


FIG. 2B



10^8
10^7
10^6
10^5
10^4
1000
100
ε'
100
1000
10^4
10^5
10^6
10^7
FREQUENCY (Hz)
NaCl
5% BENTONITE
10% BENTONITE
10% TiNT
15% TiNT

FIG. 3

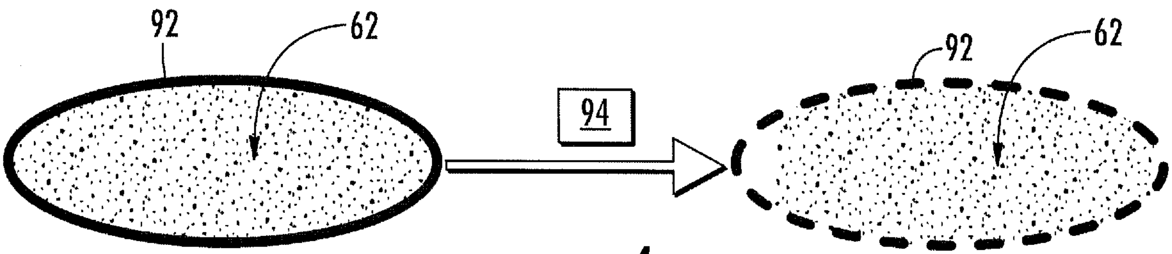


FIG. 4

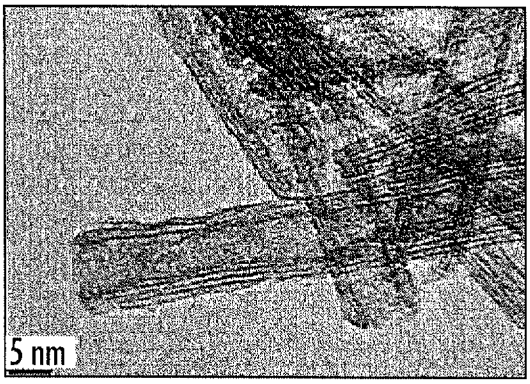


FIG. 5A

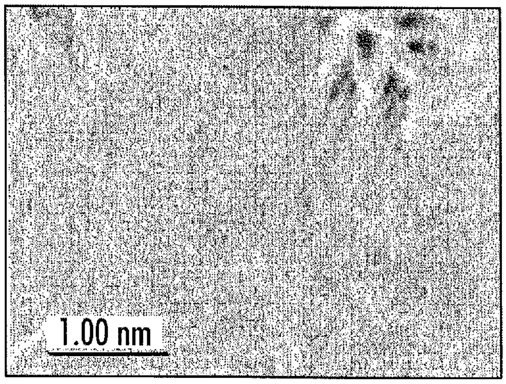


FIG. 5B

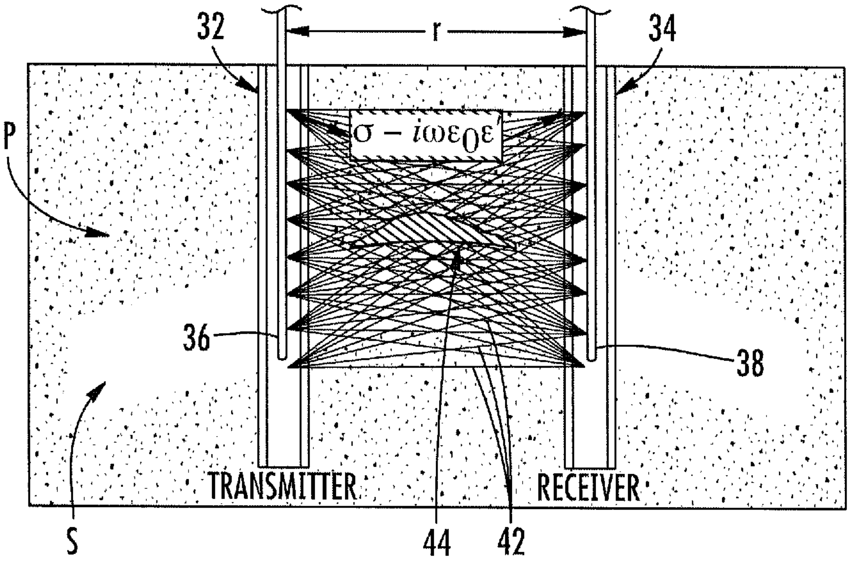


FIG. 6

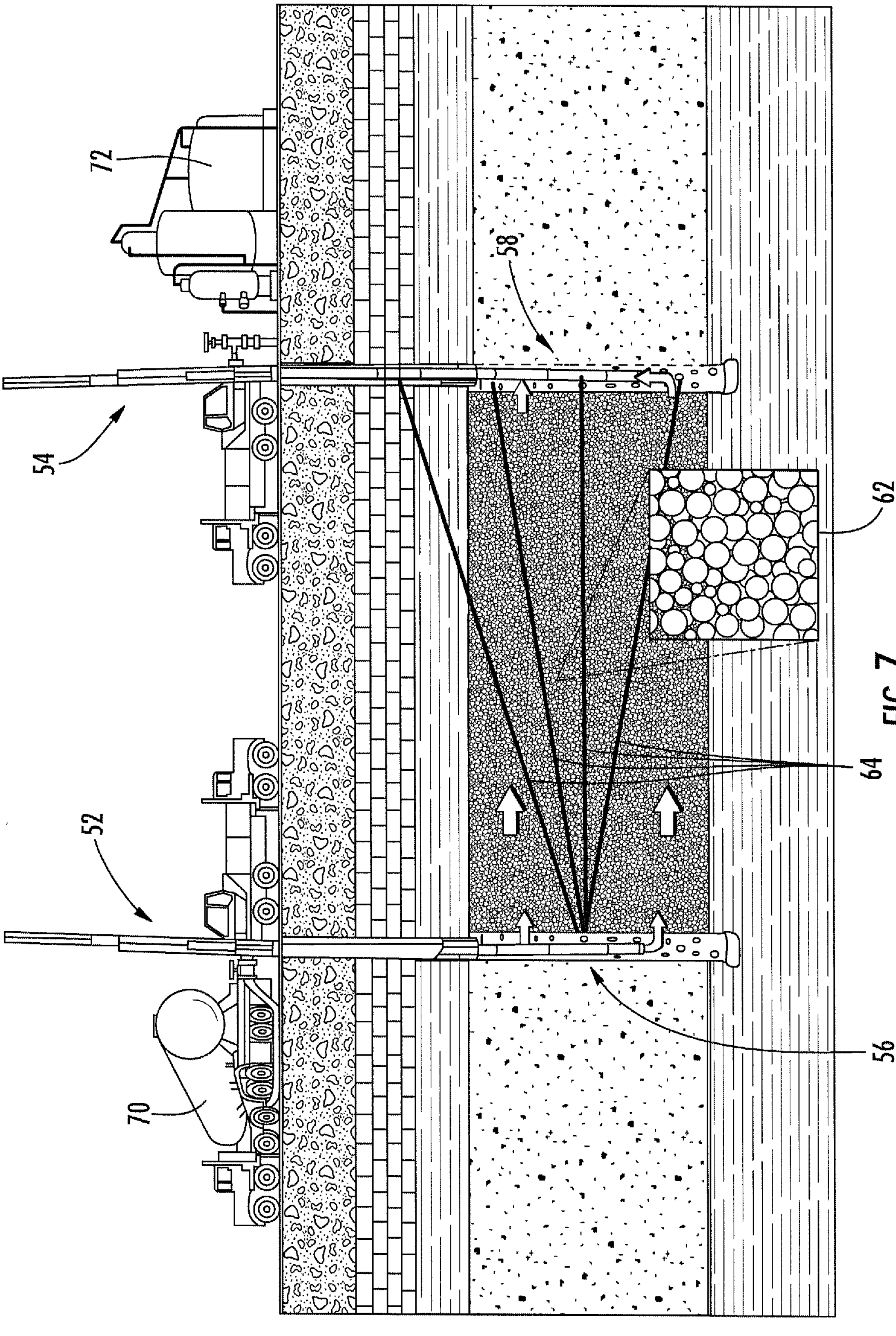


FIG. 7

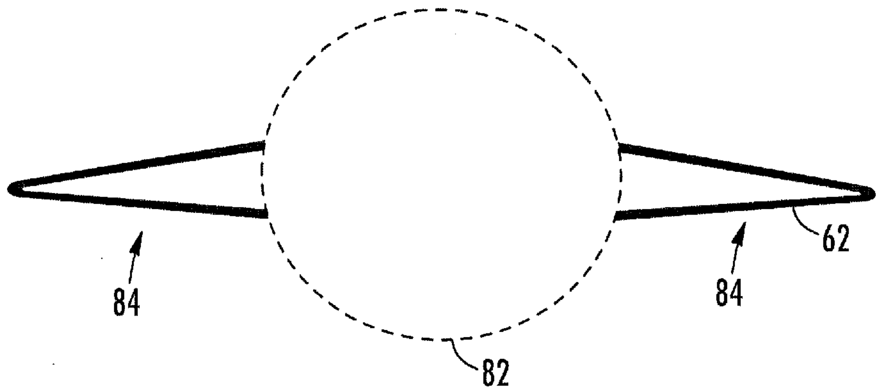


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/043603

A. CLASSIFICATION OF SUBJECT MATTER

G01V 3/26(2006.01)i, E21B 47/00(2006.01)i

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)
G01V 3/26; G21G 5/00; G06F 19/00; A61K 49/18; A61B 5/055; G01V 3/30; G01T 1/10; E21B 47/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:contrast agent, subterranean, ganglion, bypass, fracture, nanopolymorph, low-frequency, dielectric, permittivity and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0309835 A1 (BARBER et al.) 22 December 2011 See abstract, paragraphs [0004],[0022],[0026],[0035],[0044], claim 1, and figures 1,2,3A.	1,21,29-31
Y		2-5,9-14,18-20,22-25,32-36,40,41
A		6-8,15-17,26-28,37-39
Y	US 2009-0294692 A1 (BOURKE, JR. et al.) 03 December 2009 See abstract, paragraphs [0376],[0412], claim 61, and figures 43A-43D.	2-5,9-14,18-20,22-25,33-36
Y	US 2010-0286918 A1 (MOOS et al.) 11 November 2010 See abstract and claims 1,4,5.	32-36,40,41
Y	US 2009-0263331 A1 (WU et al.) 22 October 2009 See abstract and claims 1-4.	4,13
A	US 3657730 A (ROBINSON et al.) 18 April 1972 See abstract and claim 1.	1-41

☐ 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
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 August 2013 (30.08.2013)	**02 September 2013 (02.09.2013)**

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
PARK Jin Ho
Telephone No. +0424818398

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group I, Claims 1-10, 22-31 and 32-41, respectively drawn to: a method of identifying a subterranean feature during geological exploration; a method of identifying a ganglion of bypassed oil in a geological formation; and a method of illuminating a subterrain fracture.

Group II, Claims 11-20, drawn to a contrast agent suitable for use in geological applications.

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/043603

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0309835 A1	22/12/2011	WO 2011-159509 A2	22/12/2011
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		WO 2010-129677 A2	11/11/2010
		WO 2010-129677 A3	24/02/2011
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US 3657730 A	18/04/1972	None	