United States Patent [19]

Erdman

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[45] **March 6, 1973**

[54] **DETECTION OF REDUCING CONDITIONS IN A FORMATION AS IN OIL PROSPECTING**

[75] Inventor: **John G. Erdman,** Bartlesville, Okla.

[73] Assignee: **Phillips Petroleum Company**

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[52] **U.S. Cl.** .....**23/230 EP,** 324/0.5 R

[51] **Int. Cl.**.....**G01n 27/78,** G01n 33/24

[58] **Field of Search**.....23/230; 324/0.5 G, 0.5 R

[56] **References Cited**

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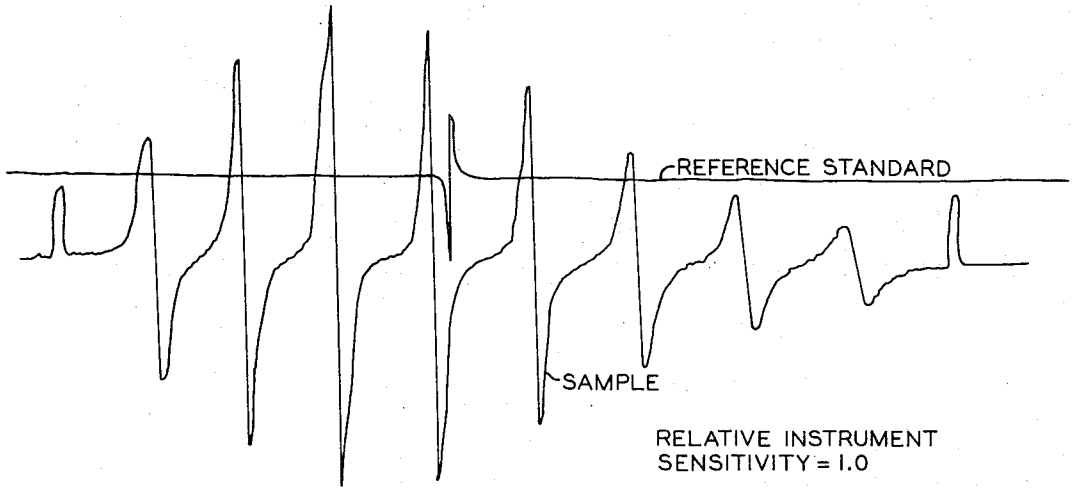
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Primary Examiner—Morris O. Wolk
Assistant Examiner—R. M. Reese
Attorney—Young and Quigg

[57] **ABSTRACT**

Reducing conditions in a formation, as in a location in which petroleum forming conditions and/or petroleum may exist, are determined by introducing into the formation or into a sample thereof a substance such as a transition metal salt solution, e.g., a +5 vanadate ion, allowing reducing conditions which may exist to reduce the selected ion, e.g., +5 vanadate, to a lower valence state, e.g., to +4 vanadyl ion, and then testing for the lower valence state ion in the formation or in the sample as by an electron spin resonance method. Crude oil bearing strata or rock or the oil itself act to reduce the ion due to the presence of quite strongly reducing organic matter which acts to convert the valence state. An additive or catalyst can be added to enhance the apparent reduction of the ion used, e.g., an organic base, for example, pyridine.

6 Claims, 12 Drawing Figures



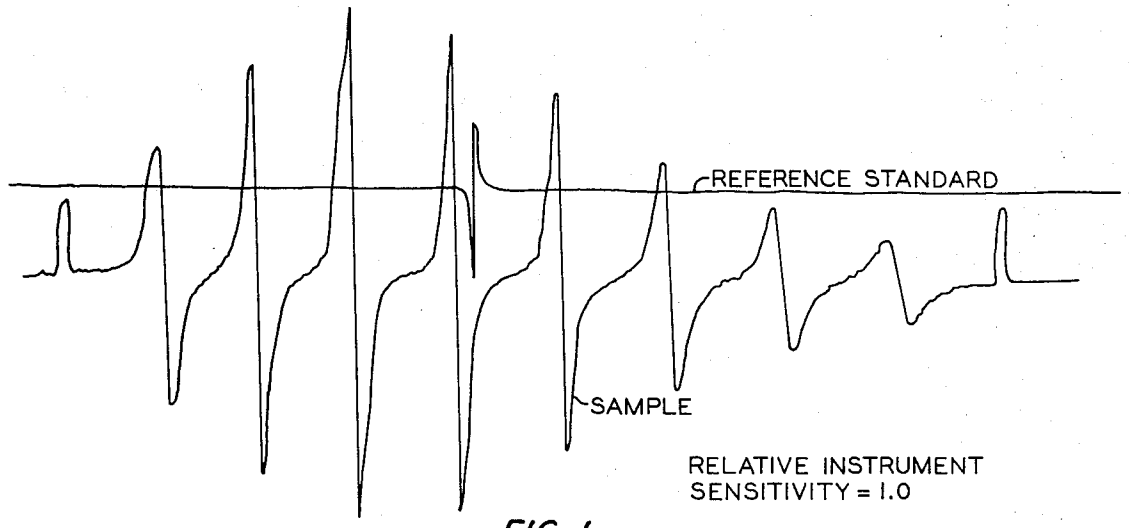


FIG. 1

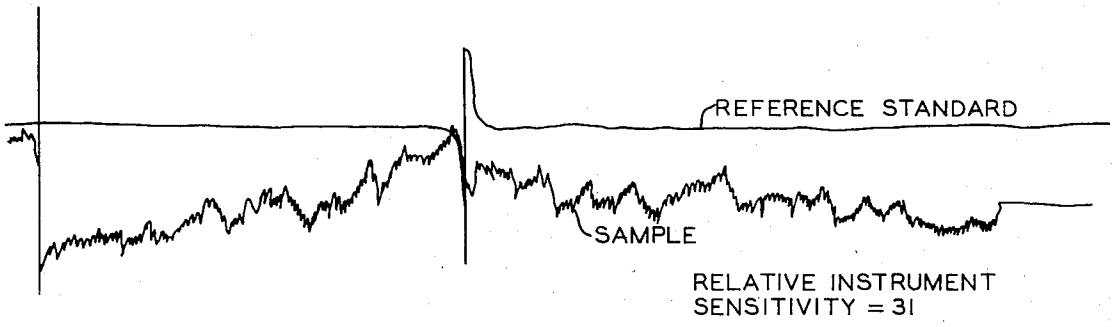


FIG. 2

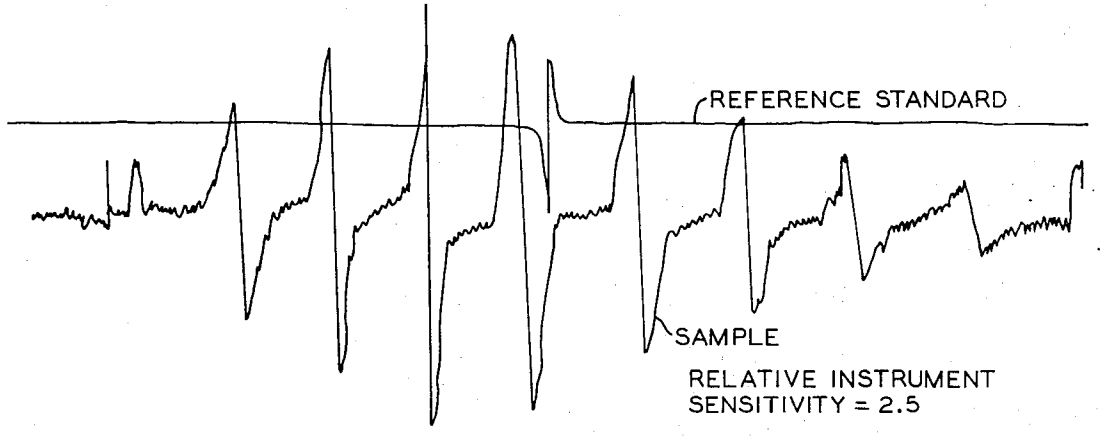


FIG. 3

INVENTOR.
J. G. ERDMAN

BY Young & Quigg

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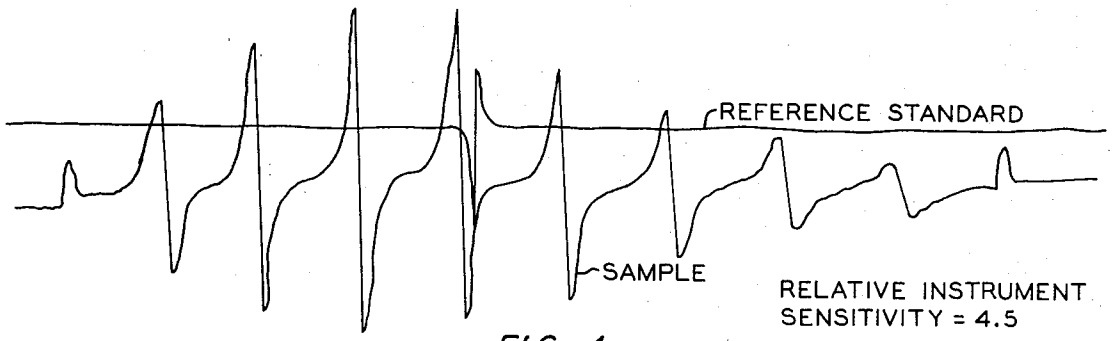


FIG. 4

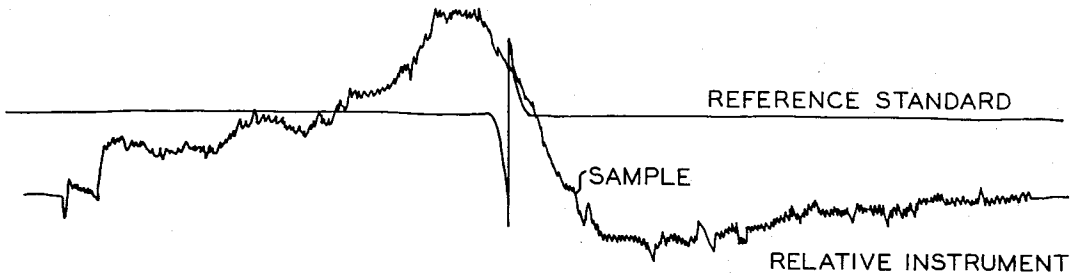


FIG. 5

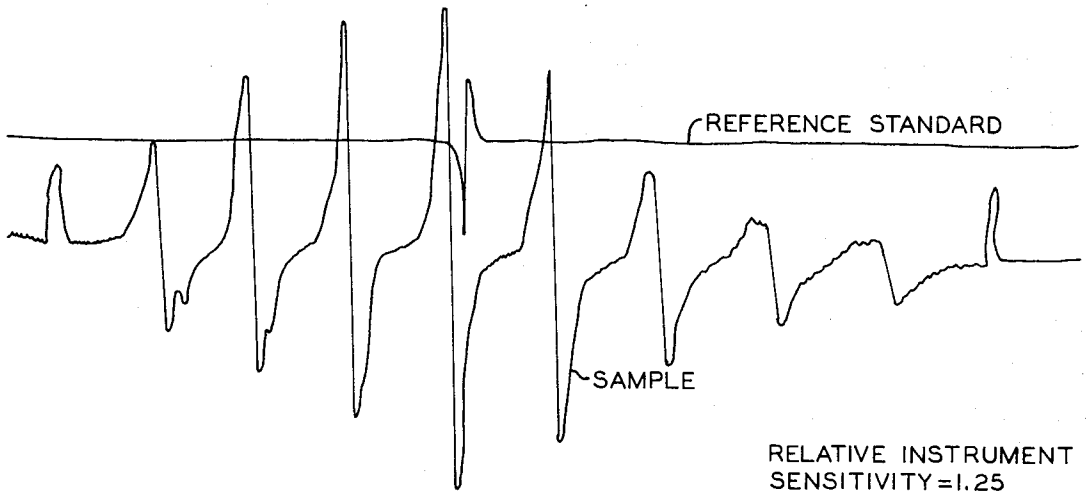


FIG. 6

INVENTOR.
J. G. ERDMAN

BY

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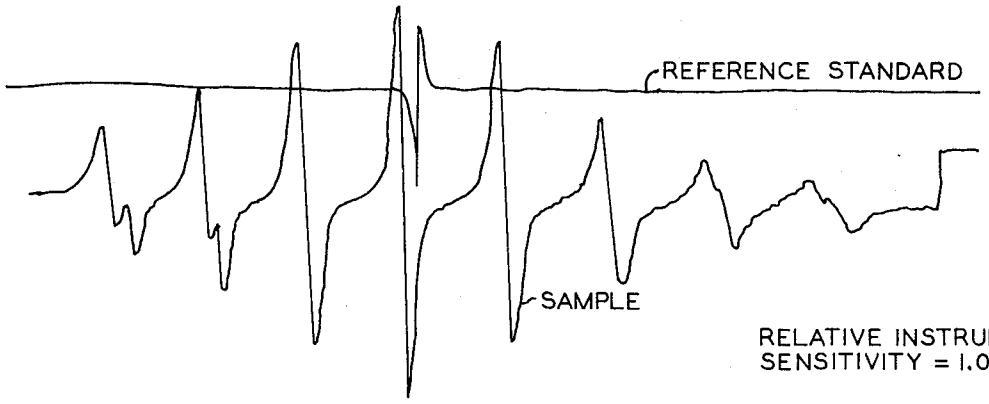


FIG. 7

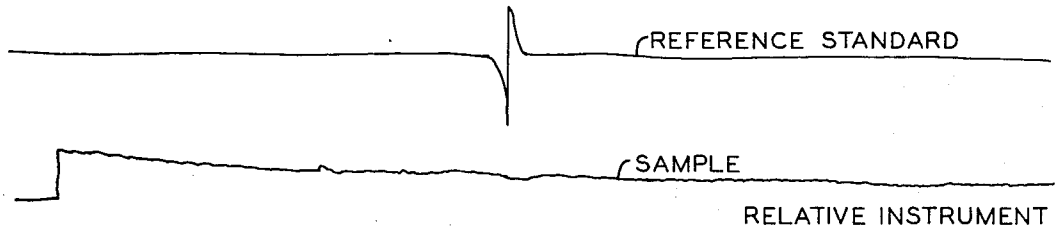


FIG. 8

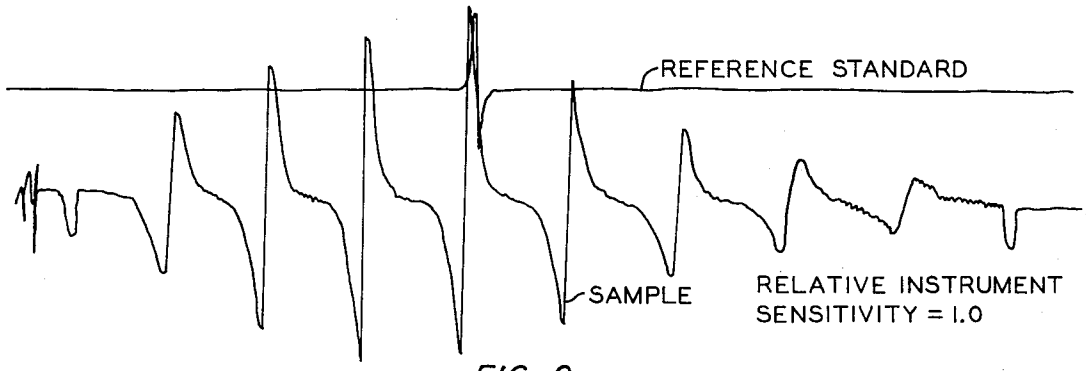


FIG. 9



FIG. 10

INVENTOR.
J. G. ERDMAN

BY

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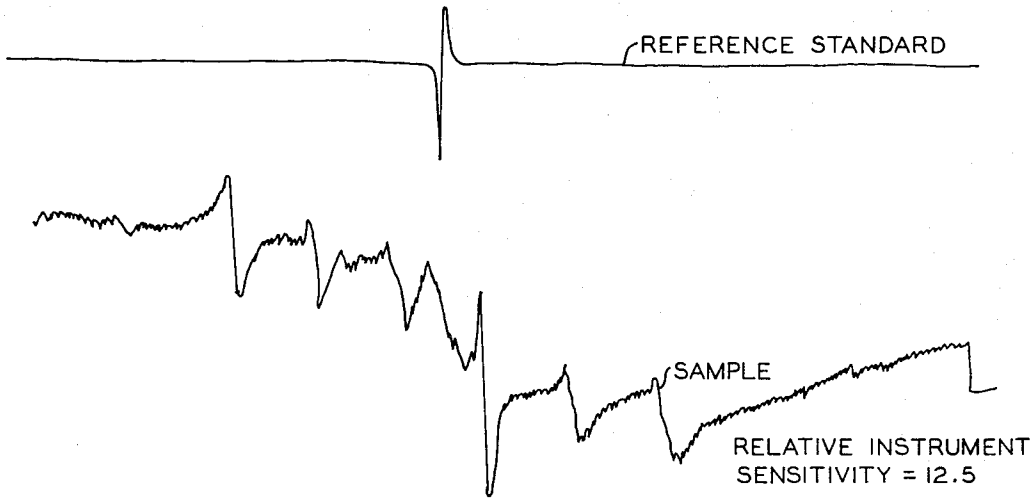


FIG. 11

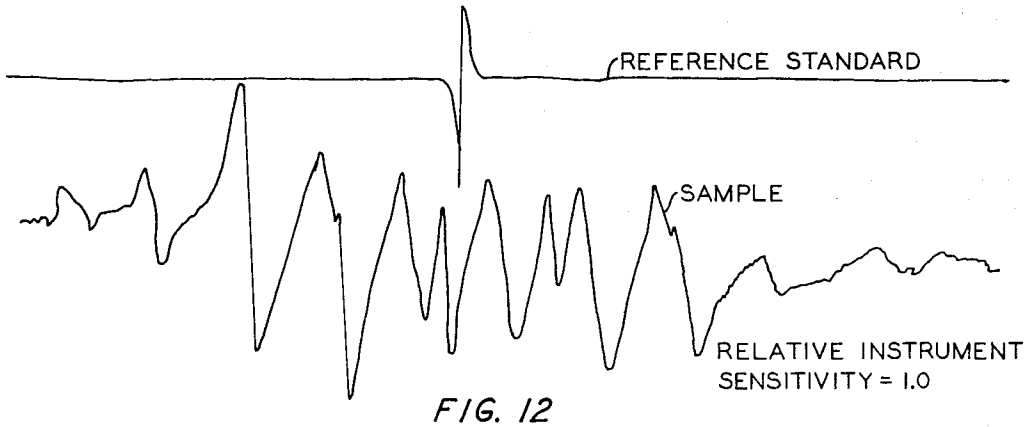


FIG. 12

INVENTOR.
J. G. ERDMAN

BY

ATTORNEYS

DETECTION OF REDUCING CONDITIONS IN A FORMATION AS IN OIL PROSPECTING

This invention relates to determining reducing conditions in a formation, as in prospecting for petroleum or similar hydrocarbonaceous materials.

In one of its concepts the invention provides a method for determining whether a formation may be a source or petroleum-containing formation by introducing a salt such as a transition metal salt, for example, vanadium salt, in solution in the +5 oxidation state into the formation and then, later, withdrawing a sample of the liquid to determine whether it has been reduced to the +4 oxidation state in the case of vanadium. In another concept of the invention determination is made by an electron spin resonance method.

It is generally known that highly reducing conditions in an organic rich sediment are quite favorable to the genesis of large amounts of crude oil. It is not unreasonable to postulate that the rate at which reducing conditions are established is one of the determining factors as to whether the organic matter deposited in a sediment has on the one hand yielded petroleum gas and/or oil in sufficient quantity to migrate and accumulate in a reservoir, or on the other hand, moved toward the family of non-migratable bitumens such as coals and oil shales. Under ordinary circumstances this reducing condition remains a characteristic of the source rock and, indeed, of oil produced from it.

Direct determination of the reducing character of a rock in a bore hole is complicated by a number of factors, for example, presence of the agents H_2S, HS^-, and $S^=$. These agents tend to poison metallic electrodes which may be sought to be employed. Further, for complex organic systems, there appears to be no simple relation between redox potential and pH. Further, in fine grained rocks appreciable streaming potentials may be developed.

It has now occurred to me that reducing facies characteristic of source beds of petroleum and, indeed, rocks which are saturated with petroleum itself might well be detected by flooding a bore hole with and forcing back slightly into the formation a solution of a transition metal ion which will be selectively reduced and which in the lower oxidation state can be determined by down-the-hole methods. Similarly, it has occurred to me that formation samples or rocks suitably protected until tested might well be tested at ground surface in similar manner as herein described.

Thus, it has occurred to me that solutions of a number of elements capable of several oxidation states and a variety of detection methods might well be employed. Specifically, the coupled vanadyl-vanadate is subjected to reducing conditions in a rock section. In such operations the couple can be considered as a sensitizing agent and the reducing conditions as a developer. An electron spin resonance measurement method can be considered as a detector.

The principle upon which the invention is based is that certain heavy metal ions may exist in several oxidation states with redox potentials such that the reducing conditions characteristic of source rocks of petroleum and crude oils will effect a transition from a higher to a lower oxidation state.

In rocks which have been oxidized and which are poor in organic matter, vanadium when naturally present or when added artificially is stable in the +5 oxidation state which at earth pH's exists as the vanadate ion. In the presence of highly reducing organic matter, such as that associated with the genesis of crude oil, or for that matter with crude oil itself, vanadium is stable only in the +4 oxidation state, that is, as vanadyl ion. The interconversion of vanadyl and vanadate is rapid under earth conditions and the salts are soluble. In the vanadate ion all the electrons are paired, whereas in vanadyl there is one unpaired electron. Accordingly, the vanadate ion is invisible on electron spin resonance scan, whereas the vanadyl ion gives a strong and characteristic signal. Detection of vanadyl is, therefore, possibly uninfluenced by varying amounts of vanadate.

Detection of petroleum source bed rocks and crude oil saturated reservoir rocks by electron spin resonance detection of the +4 vanadium naturally contained therein has been suggested, particularly in respect of high vanadium containing oils and source rocks of Venezuela. However, the designing of a suitable downhole electron spin resonance machine is a formidable undertaking and the sensitivities which must be achieved to detect the small amounts of +4 vanadium naturally contained in the rocks and oils has made the method seem insurmountable. However, by the use of a "sensitizing and development" procedure as herein described whereby, for example, the formation is flooded with electron spin resonance invisible vanadate ion and allowing the organic rich source rock and oil bearing strata to reduce the vanadate to vanadyl, an increase in signal strength of many hundreds of thousands or tens of thousands of times that naturally present in the source bed facies or oil well can be achieved. This decreases by the same factor the requirements for the detecting system.

In addition to acting as a sensitizing agent for the logging of a bore hole, such ion pairs as vanadyl-vanadate can be used to characterize rocks and to detect oil accumulation in cases where a through-formation-contact can be established between wells, i.e., where liquid normally water, forced into one well appears in the other. In such case if a solution of, for example, vanadate is forced into a porous sand which is barren throughout the path of travel to the receiver well, the liquid withdrawn therefrom will contain vanadium in the form of vanadate. If the water, however, containing the vanadate should flow under an oil accumulation or come in contact with rocks containing oil or its associated organic matter, the water issuing from the receiver well will contain appreciable quantities of vanadyl ion. Used in this way the electron spin resonance or other detector need not necessarily be sent down the hole.

It is not necessary always to force the testing liquid into a bore hole. An inert atmosphere chamber using freshly cut cores which have been protected from oxygen, e.g., in a rubber sleeve barrel, can be used at ground surface. However, as an alternate method a bore hole can be flooded with a solution of the ion which seems the most promising for it, the solution driven back into the rock formation and then sidewall cores taken. These cores would be protected until electron spin resonance measurements or other tests could be made at the surface or in the laboratory. Cross well

studies would require bottom hole samples of the fluid from the receiver well and these would be collected in suitably inert containers.

An object of this invention is to provide a method for the detection of reducing conditions in a formation. Another object of this invention is to prospect for petroleum or similar hydrocarbonaceous substances. A further object of this invention is to detect crude oil in a ground formation or in a sample taken therefrom. Further, still, it is an object of this invention to intensify the signal strength obtainable in electron spin resonance detection methods applied to the detection of certain ions in, say, reduced valence state. A more specific object still of the invention is to detect oil or oil producing conditions by using a transition metal salt, for example, vanadium salt, even under such conditions in which electron paramagnetic resonance absorption phenomenon which is believed to be due to the presence of a substantial concentration of unpaired electrons is less prominent and may be absent from certain oils.

Other aspects, concepts, objects, and the several advantages of the invention are apparent from a study of this disclosure and the appended claims.

According to the present invention there is provided a method for testing for reducing conditions in a formation or a sample thereof which comprises subjecting to the action of the formation a solution of, say, a transition metal ion which can be selectively reduced in said formation and which in the lower oxidation state can be determined by an electron spin resonance method.

When a downhole determination is made after the ion-containing solution has been in the bore hole and in the formation, a bore hole electron paramagnetic resonance detector is passed along the exposed face to determine whether the ion has been reduced. The detector will show the lower valence forms against the original clean log. Or, as already indicated, sample is brought to the surface for analysis.

My invention is completely independent from any unpaired electrons which may be present in the crude oil or which may be absent therefrom. As noted, I can increase the signal strength many hundreds or thousands, if not tens of thousands of times over that naturally present in the source bed facies or oil, thus decreasing by the same factor the requirements for the sensitivity of the detection method employed.

The invention is broadly applicable to any ion solution which can or will be appreciably reduced in the formation. Mixtures of ions can be employed.

Although vanadium salts which are soluble and which can be pumped into a sample formation or core are now preferred, solutions of salts of other elements of the transition group metals can be employed. Specifically, by the term transition group metals, I refer to and include metals of Groups IIIB, IVB, VB, VIB, VIIB, VIII, IB, and IIB, with atomic numbers of from 21 to 80, inclusive, as shown in the Periodic Table, inside back cover, Handbook of Chemistry and Physics, 45th Edition (1964), Chemical Rubber Co. Of these, I prefer those with atomic numbers of from 21 to 30, and most preferable is the aforesaid vanadium. The invention is not intended to be limited here to the exemplary recited ions.

In the case of vanadium the following indicates the change which takes place.

crude oil

VO_3^- VO^{++}

vanadate (oxidation state, +5) vanadyl (oxidation state, +4)

In the case of vanadium the change in oxidation state is accompanied by a change in color and a change in the electron spin resonance (ESR) signal. In solution VO_3— is yellow whereas $VO^{++}$is blue. In VO_3— the V^{+5} atom has all its external electrons paired hence gives no ESR signal whereas in VO^{++} the V^{+4} atom has an unpaired external electron and yields a characteristic signal as shown in FIG. 1 which comprises part of Example I. Although color is a sensitive indicator of the oxidation state, color is easily masked by foreign substances likely to be encountered in practical field application. The ESR signal has equal or better sensitivity and is less subject to interferences. Accordingly a series of experiments have been performed to (1) demonstrate the reactions which will be involved in the use of vanadium as a geochemical indicator in petroleum exploration, (2) to compare color and ESR as indicators of the vanadium species, and (3) to demonstrate that the vanadate-vanadyl couple can indeed be used to detect crude oil in the presence of typical drilling mud formulation.

Example II shows that at the concentrations of vanadium needed as an indicator, there is no danger of loss of vanadyl by precipitation. Thus as will be discussed later, a mud-free solution of alkaline vanadate can be used as a test solution. Although the alkalinity prevents vanadyl from exhibiting an ESR signal, the signal can be brought out by neutralization with acid.

In early experiments vanadate solutions were prepared by dissolving vanadium pentoxide in aqueous sulfuric acid or in aqueous potassium hydroxide and then adding excess sulfuric acid. The former procedure is slow and the latter requires several steps. In Examples III and IV are given now preferred methods whereby readily soluble vanadyl sulfate dihydrate is dissolved in water and oxidized to the vanadate with excess potassium chromate—

$$3\,VO^{++} + CrO_4^{=} + 6\,H_2O \rightarrow 3\,VO_3^- + Cr^{+3} + 4\,H_3O^+$$

or sodium hypochlorite —

$$2\,VO^{++} + OC1^- + 7\,H_2O \rightarrow 2\,VO_3^- + C1^- + 6\,H_3O^+.$$

The latter which simply involves the use of common commercial bleach gives an ESR spectrally cleaner solution. As disclosed later, however, both chromate and hypochlorite would have preferred uses in field applications of the proposed detection methods.

Hydrogen sulfide is occasionally encountered in natural gas and crude oils. On contacting an alkaline solution, such as drilling mud filtrate the hydrogen sulfide is reversibly converted to acid sulfide, HS^- and sulfide, $S^=$. H_2S, HS^- and $S^=$ are strong reducing and complexing agents, and there was concern that (1) they might form insoluble vanadium salts, (2) form stable

complexes with mixed oxidation states of the vanadium which might give complex ESR spectra and from which the vanadyl-vanadate couple could not be easily regenerated, in other words, that H_2S, HS^-, $S^=$ might act as a poison. The experiments which form Example V show that none of these adverse effects occur at the concentrations which would be used in this invention. Instead H_2S, HS^-, $S^=$ acts as a simple reducing agent for vanadate taking it to vanadyl without precipitating it, and that the H_2S can be released and the ESR signal for vanadyl induced by the addition of acid.

Finally in Example VI is demonstrated (1) the preparation of vanadate containing drilling mud formulation, (2) the reduction of the vanadate to vanadyl by contact with a typical crude oil, Alamein crude from Egypt, and (3) successful monitoring of the indicator reaction with ESR without removal of the suspended clay and barite and without masking of the blue color of vanadyl by colored drilling mud additives such as lignosulfonates.

1. Recognition of Source Rocks or Crude Oil Pays in the Course of Drilling:

In this case a drilling mud is made up containing sufficient vanadium as vanadate to be detectable by ESR if reduced to the vanadyl state. The vanadium containing mud, which henceforth is referred to as an indicator mud, is prepared by adding to a standard drilling mud formulation 0.002 to 2 g/l. (approximately 0.0014 to 1.4 lbs/barrel) of vanadyl sulfate dihydrate. Assuming that the drilling mud formulation contains potassium or sodium dichromate as an anticorrosion agent, sufficient sodium hypochlorite (common bleach), or the less expensive calcium hypochlorite, is added to convert the vanadyl to vanadate. In the course of the drilling, samples of the drilling mud are taken periodically, acidified and checked for vanadyl by ESR. Additional hypochlorite is then added to suppress the vanadyl. A log of the rate of consumption of hypochlorite as a function of depth is then plotted. A low rate of consumption indicates little or no source rocks. A high rate of consumption would indicate source rock, oil containing reservoir rock or rock containing sour gas. A check for hydrogen sulfide evolution during and just immediately prior to the ESR scan determines whether sour gas has been encountered. A check of cuttings distinguishes between the fine ground shale or limestone which is a necessary but not sufficient requisite of a source rock and a porous sandstone or carbonate which would be an oil reservoir. An alternate method is to check the mud with an ultraviolet lamp for the fluorescence associated with crude oil.

With the exception of checking cuttings or the mud for fluorescence the entire operation can be made continuous and automatic, the data being recorded on a strip chart. The system also can provide a signal to alert the well geologist or driller to check cuttings or the mud for fluorescence.

2. Recognition of Source Rocks or Crude Oil Pays After a Hole is Drilled:

Specific formations can be tested using the standard drill stem test tool. Packers are set to isolate the formation. If casing is in place it will have to be perforated. To the drill stem is then added a solution of vanadate ion plus a small excess of oxidant preferably hypochlorite. If the formation is suspected of containing carbonates, the solution should be neutral to slightly alkaline, that is not acid. If the solution column is not sufficient to drive some of it into the formation additional pressure is applied with a pump. The pressure is then reduced (may require reducing the column of liquid in the drill stem) to allow the indicator solution forced into the formation to be expelled. This fraction of the indicator fluid is recovered either by flowing the formation or in the case of fine grained rocks reversing out. Evaluation of the formation is made by ESR examination of the recovered indicator fluid.

EXAMPLE I

This example demonstrates the characteristic signal of the vanadyl (oxidation state +4) ion.

A solution of vanadyl sulfate, $VOSO_4 \cdot 2H_2O$ was prepared in deionized water. Concentration was 0.0033 FW (formula weight) or 0.67 g/l. The solution was transferred to a 3 mm quartz tube and scanned using a Varian Associates V 4500 – 10 A ESR spectrometer. In the drawings the several charts are to be read together with the examples. Relative instrument sensitivities are provided on each chart. For approximate quantitative comparison, the sample signal amplitude should be divided by the relative instrument sensitivity.

In FIG. 1 the characteristic derivative spectrum of V^{+4} is shown.

EXAMPLE II

This example demonstrates the effect of alkaline conditions on the color and ESR spectrum of vanadyl ion.

To 2 ml of a 0.01 FW aqueous solution of $VOSO_4 \cdot 2H_2O$ there was added 0.2 ml of a 0.5 FW solution of NaOH and 3.8 ml of water. On addition of the excess of alkali, the color changed from clear blue to clear amber brown. There was no indication of turbidity. FIG. 2 shows that the addition of excess alkali at low vanadyl concentrations, though it does not precipitate the vanadium it does obliterate the characteristic ESR vanadyl ion signal.

EXAMPLE III

This example demonstrates that excess chromate ion will oxidize reversibly vanadyl ion to vanadate.

Part A: To 2 ml of a 0.01 FW aqueous solution of $VOSO_4 \cdot 2H_2O$ (pale blue) was added 0.4 ml of a 0.1 FW solution of K_2CrO_4 (bright yellow) and 3.6 ml of water. The final color was yellow and could have been from the chromate or from newly formed vanadate which also is yellow. The mixture was scanned in the ESR spectrometer 20 minutes after mixing, FIG. 3, and again after 2 hours, FIG. 4. The traces show that oxidation of approximately 70 percent of the vanadyl had taken place in the first 20 minutes, and that oxidation of the vanadyl was 85 percent complete after 2 hrs.

Part B: To 2 ml of a 0.01 FW aqueous solution of $VOSO_4 \cdot 2H_2O$ was added 2 ml of a 0.1 FW solution of K_2CrO_4 and 2 ml of water. The solution is yellow. The mixture was scanned in the ESR spectrometer about 10 minutes after mixing. FIG. 5 shows that the ESR spectrum of V^{+4} has disappeared and the spectrum of chromic ion, Cr^{+3}, has appeared; accordingly, the vanadyl has bee completely oxidized to vanadate by the amount of chromate used.

Part C: To the above solution was added 8 mg of ascorbic acid, an organic reducing agent. Despite the excess chromate, the vanadyl signal is partially restored; that is, the oxidation of vanadyl to vanadate by chromate ion can be reversed by an organic reductant. Addition of a few drops of 0.5 FW sulfuric acid strengthened the vanadyl signal, FIG. 6, indicating approximately 80 per cent regeneration of VO^{++}.

EXAMPLE IV

This example shows or determines that hypochlorite (commercial bleach) will oxidize reversibly vanadyl ion to vanadate.

Part A: To 2 ml of a 0.01 FW aqueous solution of $VOSO_4 \cdot 2H_2O$ was added 0.2 ml of a 0.35 FW solution of NaOCl and 3.8 ml of water. On addition of the colorless sodium hypochlorite solution to the pale blue vanadyl sulfate solution, the color turned deep yellow indicating oxidation of the vanadyl ion to vanadate ion.

Part B: To the above solution was added 1 ml of of 0.1 FW solution of ascorbic acid and a few drops of 0.5 FW sulfuric acid. The pale blue color of the vanadyl ion and the vanadyl ESR spectrum was restored. The signal recorded in FIG. 7 shows 96 percent regeneration of vanadyl.

EXAMPLE V

This example demonstrates that sulfide ion will neither precipitate nor irreversibly alter vanadyl ion.

Part A: To 2 ml of a 0.01 FW aqueous solution of $VOSO_4 \cdot 2H_2O$ was added 2 ml of a 0.05 FW NaOH solution, 0.2 ml. of a 0.1 FW $Na_2S \cdot 9H_2O$ and 1.8 ml of water. The blue solution darkened on addition of the base, that is turned from blue to amber but remained clear. On addition of the sulfide solution the color became dark amber but remained clear indicating that at these concentrations the sulfide does not precipitate the vanadium. The ESR spectrum, FIG. 8, is blank indicating that the alkaline sulfide does not further reduce V^{+4} or form a free radical complex which would exhibit an ESR signal.

Part B: A solution identical to that in Part A was prepared except that 1 ml less water was added. After standing for 1 hour 1 ml of 0.5 FW H_2SO_4 was added to neutralize the alkali and release the sulfide as hydrogen sulfide. The solution turned from dark amber to pale blue and as shown by FIG. 9, 64 per cent of the ESR signal is restored.

EXAMPLE VI

This example demonstrates a convenient method for establishing a dilute solution of vanadate ion in a typical drilling mud formulation; that it can be reduced to vanadyl by contact with a crude oil; and that the presence of the vanadyl in the mud can be recognized by ESR.

Part A: To 2 ml of a typical drilling mud formulation was added 2 ml of 0.01 FW aqueous solution of $VOSO_4 \cdot 2H_2O$ and 2 ml of water. As shown in FIG. 10 the ESR vanadyl spectrum disappears, the weak peaks in the trace not corresponding to those of vanadyl. Disappearance of the vanadyl spectrum is attributed to the alkalinity of the drilling mud and probable partial oxidation of vanadyl to vanadate.

Part B: To 2 ml of the same drilling mud formulation was added 2 ml of 0.01 FW $VOSO_4 \cdot 2H_2O$, 0.2 ml of 0.1 FW K_2CrO_4 and 2 ml of water. By adding the chromate oxidation of the vanadyl to vanadate was assured. The ESR spectrum, FIG. 11, is essentially the same as in FIG. 10.

Part C: The mud-vanadate slurry from Part B was mixed with 1 ml of a medium gravity crude oil, allowed to stand for 0.5 hours and then 2 ml of 0.5 FW H_2SO_4 added to neutralize the alkali in the drilling mud formulation. FIG. 12 shows that the crude oil reduced the excess chromate and the vanadate, the latter back to vanadyl, and that the ESR spectrum could be made to appear by addition of acid. Although bands are present in the spectrum which stem from the drilling mud and the reduced chromate these bands do not mask those of the vanadyl.

In order to enhance the apparent reduction of valance which takes place in the operation of the method of the invention, there can be added an additive or catalyst, e.g., an organic base, for example, pyridine. Thus, the additive or catalyst enhances the apparent reduction of the ion used.

Reasonable variation and modification are possible within the scope of the foregoing disclosure and the appended claims to the invention the essence of which is that reducing conditions in a formation likely to contain petroleum or petroleum forming conditions are determined by passing into the formation or into a sample thereof a solution containing an ion, the valence state of which will be changed by such reducing conditions and the change in state of valence of which can be detected as by an electron spin resonance method.

I claim:

1. A method for detecting reducing conditions present in a formation in which petroleum may exist which comprises introducing into the formation or into a sample thereof a transition metal as a salt solution thereof, the valence state of which will be reduced if reducing conditions exist indicating the possible presence of petroleum, and of which the reduced valence state can be detected by an electron spin resonance or electron paramagnetic resonance method and then detecting whether reducing conditions exist by testing for the valence state of said metal in said solution.

2. A method according to claim 1 wherein the metal is an element having an atomic number in the range 21–30.

3. A method according to claim 2 wherein the metal is vanadium and its valence is changed from +5 to +4 when said reducing conditions exist.

4. A method according to claim 1 wherein an additive or catalyst is added to enhance the apparent reduction of valence.

5. A method according to claim 4 wherein an organic base is used.

6. A method according to claim 5 wherein said organic base is pyridine.

* * * * *