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METHOD OF PETROLEUM EXPLORATION

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The invention relates to the art of exploring for subterranean oil deposits and has more particular reference to petroleum exploration by analysis of earth, drilling mud or water samples.

Deposits of hydrocarbon material such as natural gas and petroleum oil are retained at a considerable depth within the earth and are therefore under a tremendous pressure. However, since the overlying earth formations are permeable to the infiltration and diffusion of such hydrocarbon gases as are thus trapped, the said gases find their way to the surface and it is now recognized in geochemical prospecting that the diffused gases appearing at the surface are due to valuable subterranean deposits.

In a number of methods for detecting said subterranean deposits it has been proposed to evolve the hydrocarbon gases from the soil samples taken near the surface of the earth and analyze said evolved gases for constituents related to the deposits sought. These methods of prospecting, based on gas analyses of leakage products from buried deposits, have been used notwithstanding some difficulties which are inherent in the methods themselves. In exploring for petroleum oil such methods leave much to be desired since it is difficult to distinguish a natural gas field from a petroleum oil field or other source of hydrocarbon.

A more recent method for locating petroleum oil is disclosed and claimed in the patent to John G. Campbell, No. 2,227,438 granted January 7, 1941 and entitled Method of determining the petroleum oil content of earth samples. The invention of said patent is based on the physical phenomenon that petroleum oil has a fluorescent appearance under ultra-violet light. Drill cuttings, cores and other earth samples are first dried in accordance with the disclosure in said application and then ground to a predetermined fineness. An oil solvent is used in the extraction step for extracting the oil from the dry earth sample and the oil content of the extract is then determined by subjecting the said solution to ultra-violet light to cause the oil content thereof to fluoresce. The intensity of said fluorescent effect is in direct proportion to the oil content of the solution thus analyzed, and by measuring the said fluorescent effect a quantitative determination can be made of the petroleum oil content of the extract and thus of the earth sample. Drying and grinding of samples of any wet material prior to extracting is standard practice in analytical chemistry. In the present invention the drying and grinding of the earth samples are not necessary since the invention is based on a discovery of the peculiar manner in which the oil is contained on the sedimentary particles. In fact, the drying of the earth samples will reduce the accuracy of the oil determination.

The invention, therefore, has for an object to provide an improved method of exploring for buried petroleum deposits by analysis of earth samples.

Another object is to provide a petroleum exploration method by analysis of earth samples which will eliminate the step of drying the wet earth samples and which will make possible a more accurate determination of the oil content thereof as a result.

Another object of the invention is to provide an improved method of analyzing earth samples to quantitatively determine the oil content thereof and wherein the samples in their wet condition are subjected to an extraction step using an oil solvent.

In addition to quantitatively determining the oil content of wet earth samples the method may be applied to the drilling fluid leaving or entering the well and to surface waters found in the vicinity of oil producing areas. The extraction step has utility in separating the oil from the water to which the same is adsorbed, or, in which it is dissolved or suspended therefore, insofar as the present method is concerned the water may comprise a film surrounding an earth particle or the water making up the drilling fluid or surface water containing oil. It is contemplated that the extraction step by means of an oil solvent will have application to all aspects of the invention and a major advantage, particularly in connection with the drilling fluids and surface waters, is that the extraction step leaves behind any salts which may fluoresce under ultra-violet light.

Another object of the invention resides in a method of extracting a fluid containing oil such as drilling muds from rotary wells or surface waters in the vicinity of oil producing areas and which is based on the discovery of the manner in which the oil is contained in the fluid and which therefore requires an oil solvent having certain characteristics with reference to the said oil which is to be extracted by the oil solvent.

The reason why it is possible by the present method to eliminate the drying step in the analysis of earth samples and why said earth samples may be extracted in their wet condition by an oil solvent can best be understood by considering the

mechanism of the migration of oil from a subterranean pool to the surface of the ground.

Oil deposits are overlain by a relatively impermeable cap-rock. This cap-rock is impermeable to any major migration of oil or gas from the oil pool. Usually an oil pool has a gas-cap lying between the oil and the cap-rock. The oil is usually underlain by water. The sedimentary particles composing the cap-rock and the sediments overlying the cap-rock have adsorbed films of water, excepting where conditions have destroyed the films by evaporation. Some constituents of the oil, which have the ability of spreading on water, spread on the adsorbed water films on the sedimentary particles and thus these oil constituents migrate to the surface of the ground as monomolecular films. In the Campbell method of exploring for oil as disclosed and claimed in the patent herein identified the oil which is extracted from the earth samples, is the oil above referred to as spread on the adsorbed water films on the earth particles. The spreading of one liquid on another liquid is a well recognized phenomenon. Tests have been made to show that the speed of this spreading can be as great as 20 cms. per second.

The generally accepted theory of the mechanism of spreading of one liquid over another is based on the fundamental theory of the molecular structure of matter. According to this theory, the molecules of matter are in a state of motion, being freer to move in gas than in a liquid and freer to move in a liquid than in a solid. When a liquid is placed on another liquid having a higher specific gravity, some of the molecules of the upper liquid are adsorbed by the molecules of the lower liquid. If the force of cohesion of the molecules of the upper liquid is less than the force of adhesion of the molecules of the upper liquid to the lower liquid, the molecular motion of the molecules of the lower liquid to which the molecules of the upper liquid adhere will tear apart the molecules of the upper liquid from one another so that the upper liquid will spread over the lower liquid to form a mono-molecular film. If the force of cohesion of the molecules of the upper liquid is greater than the force of adhesion of the molecules of the upper liquid to the molecules of the lower liquid, the upper liquid will not spread on the lower liquid. Spreading of a liquid on a solid can not occur to the extent that a liquid spreads over another liquid, because of the smaller freedom of motion of the molecules of the solid.

In the method as heretofore practiced for analyzing earth samples to determine the oil content thereof, the step wherein the earth samples were dried and then ground to relatively fine particles, had the effect of destroying the adsorbed water films to which the oil films are adsorbed. As a result, the oil was adsorbed directly to the earth particles, thereby preventing the complete extraction of the oil from the dried earth particles. By reason of the recognition of the mechanism by which the oil is contained on the earth particles, we have perfected a new and novel procedure for determining the oil content of the earth particles, which depends on extracting the samples with a suitable solvent without first drying and grinding, and at the same time we obtain a more complete extraction of the oil from the earth samples.

In another patent granted to John G. Campbell on February 16, 1943, No. 2,311,151 entitled Analysis of soil samples for determining the oil content, a method is disclosed and claimed for adjusting the oil content results to allow for variations in the surface area of the particles comprising the earth samples. The invention of said patent resides in the provision of a factor for surface adjustment whereby the results obtained in measuring the fluorescence of the extract under ultraviolet light could be adjusted to compensate for the variations in the surface area of the particles making up the earth samples from which the extract was obtained. An important step in the present improved method resides in the fact that the oil contained in the earth samples can be extracted from said samples while said samples are in a wet condition, and accordingly, a more simplified procedure can be followed for determining the oil content of earth samples which eliminates the necessity of adjusting for the surface area of the particles comprising a sample. Because of the much greater surface area of the fine particles in a sample, the greater portion of the oil in the sample is adsorbed on the water layers adsorbed on these fine particles. The purpose of analyzing earth samples for oil is not to determine the absolute oil content of the sample but to determine the relative oil content in comparison with other samples from the same area that have been analyzed by the same procedure. We have found that if the earth sample is dispersed in water and the dispersion subjected to centrifugal force for a definite period of time the large particles of the sample are separated from the fine particles. By analyzing the water suspension of the fine particles for oil and also determining the solid content of the suspension, the oil content per unit of the fine material can be determined. While variations in the proportion of the various sized particles composing the suspension of fine particles will cause variations in the surface area, the error introduced by this factor is not of sufficient magnitude to materially affect the results. In order to desorb the oil adsorbed to the water films which are adsorbed to the earth particles, we use oil solvents having certain characteristics with reference to the oil being extracted.

The purpose of analyzing drilling-fluid for oil is to determine the increase in the oil content of the drilling-fluid leaving a drilling well occasioned by the dispersion of a portion of an oil-bearing horizon in the drilling-fluid. The drilling action results in a dispersion of a portion of the oil-bearing horizon in the drilling fluid. This dispersion is equivalent to the dispersion which we obtain in the laboratory in dispersing the earth samples in connection with analyzing them by our method.

Surface waters such as wells and springs in the vicinity of oil producing areas contain oil throughout the body of the water. This oil can be approximately determined qauntitatively by measuring the intensity of the fluorescent effect produced when the water itself is subjected to the action of ultra-violet light and comparing the results with the intensity of the fluorescent effect produced by standard solutions of petroleum oil under similar treatment. However, salts may be present in the water which will fluoresce under ultra-violet light and a fictitious oil value would be determined. We have found the procedure of extracting the oil from the water by means of a solvent and then subjecting the extract to the action of ultra-violet light to determine the intensity of the fluorescence produced by the oil in the extract, to be a more desirable method.

As previously stated, the oil present in earth samples, drilling fluid, and water with which we are primarily concerned in our process of locating and developing oil deposits is the oil adsorbed to water. In these samples the oil is present in practically unweighable amounts and said oil may be termed adsorbed oil since the same has an adsorbed relation with the water molecules. The force with which the oil adheres to water molecules can be measured by the work required to separate the oil from the water. This work is represented by the equation

$$W_{AB}=Y_A+Y_B-Y_{AB}$$

where

W_{AB} equals the work to separate the oil from the water in ergs per sq. cm.

Y_A equals the surface tension of the oil in dynes per sq. cm.

Y_B equals the surface tension of water in dynes per sq. cm.

Y_{AB} equals the interfacial tension between the oil and water in dynes per sq. cm.

Since the work of adhesion of the oil to water was sufficiently great to overcome the cohesion of the oil molecules for each other so as to permit the spreading of the oil on the water, the oil can only be separated from the water by the use of a relatively water-insoluble oil solvent which has a work of adhesion to water greater than the work of adhesion of the oil to water. The work of adhesion of paraffin hydrocarbons, the principal constituents of petroleum oil, is from 36 to 48 ergs per sq. cm. at 25 degrees centrigrade. Therefore, the solvent used to extract the oil from the water should have a work of adhesion to water in excess of 36 ergs per sq. cm. at 25 degrees centigrade. We have found that benzene with a work of adhesion to water of about 66 ergs per sq. cm. and ethyl ether with a work of adhesion to water of about 78 ergs per sq. cm. each extract more oil from the same sample than does petroleum ether. Since petroleum ether is composed of paraffin hydrocarbons, its work of adhesion to water is practically the same as the oil. Therefore low results are obtained when the sample containing adsorbed oil is extracted with petroleum ether. The use of an oil solvent having a work of adhesion to water of more than 36 ergs per sq. cm. may be termed method No. 1.

We have found that the addition of water soluble substances having a slight solvent action for petroleum oil will result in the more complete removal of the oil adsorbed to the water by the oil solvent. We have added water miscible liquids such as acetone, methyl glycol, ethylene glycol, and diethylene glycol monoethyl ether to the water to be extracted and have obtained higher oil results when the sample was extracted with benzene than when none of the above liquids were used. We desire to use as little of the water miscible materials as possible because of unfavorable factors that develop when large quantities of the same are used. There are present in some earth samples materials other than oil which produce a fluorescent appearance when subjected to the action of ultra-violet light. Some of these materials are slightly soluble in the water miscible liquids, and therefore, when present in the earth sample, a portion of these materials is in the extract that is subjected to the action of ultra-violet light, thus producing a fictitious oil value. These fluorescent materials are present in the extract examined because the water miscible liquid is distributed between the water layer and the solvent layer. The procedure of adding a water miscible substance having a slight solvent action for petroleum oil to the water to be extracted in termed method No. 2.

A procedure which we have found satisfactory for extracting the adsorbed oil from wet earth samples, for example, in accordance with the above outline, is as follows:

The sample is first of all mixed with a water solution of a dispersing agent such as hexametaphosphate or sodium pyrophosphate. The amount of earth varies between wide limits due to its clay content, but we try to judge the amount of sample to solution so that about 25 grams of the dispersed phase following the centrifugal action, to be subsequently described, contains about 5 to 7 grams of solids in suspension. The total volume of suspended solids and liquid is about 125 cc. This dispersion is conveniently carried out by any conventional shaking machine with the solution and sample being contained in a screw-capped jar or other suitable container. The fluidity of the dispersed phase of the earth sample will preferably resemble a thin slurry. The time required to disperse the sample varies with the characteristics of the sample, sandy type of earth particles requiring less time than clayey types. The time required varies from thirty minutes to a number of hours. From this point on the procedure for analyzing earth samples and drilling fluid is the same.

After the sample is practically dispersed, the jar and contents are subjected to centrifugal action for a period of time sufficient to separate any coarse material from the dispersed phase. The centrifugal force used should be the same for any given length of time to obtain comparable results. About 25 grams of the uniform dispersed phase are placed in a suitable screw-capped jar, the upper half of which is preferably graduated in milli-liters divisions. An oil solvent is then added to the dispersed phase in the jar and the same is agitated for a period of time sufficient to extract the oil from the dispersed phase of the earth sample.

In accordance with method No. 1, as previously described, the oil solvent should be relatively water-insoluble and the same should have a work of adhesion to water of more than 36 ergs per square centimeter. Examples of such an oil solvent are benzene and ethyl ether. Following agitation of the contents within the jar the same is then placed in a centrifugal machine and whirled for about a minute, or, until the solvent separates from the water. This separation of the solvent from the water would result in time but the action of the centrifugal machine speeds up the separation.

According to method No. 2, the above procedure is followed in connection with either the dispersed phase of the earth samples, the relatively cutting-free drilling fluid, or water such as surface water suspected of containing oil, with the exception that a water soluble substance having a slight solvent action for petroleum oil is added to the jar containing the sample being analyzed together with the oil solvent. While a considerable number of substances can be used to facilitate removal of the adsorbed oil, the efficiency of oil recovery by the use of a water-insoluble oil solvent is not the same in all instances. This is illustrated by the results given below obtained when using benzene with various water miscible substances on the same earth

dispersion. The results obtained using benzene and ethyl ether separately without the addition of water miscible substances are also given for purposes which will become apparent. The action of these water miscible substances having a slight solvent action for petroleum oil is probably due to their entering the interface between the adsorbed oil and the water adsorbed to the earth particle, thus permitting the easier removal of the oil by the oil solvent becoming adsorbed to the water. This replacement of the oil by the oil solvent becomes possible because the work of adhesion of the oil solvent to water is greater than the work of adhesion of oil to water.

About 25 grams of an earth dispersion were used in each of the tests given below. This dispersion consists of 5.5 grams of earth and 19.5 grams of water. The oil results obtained were corrected by blank determinations.

Test No.	Treatment	Volume oil solvent	Oil parts per million
		Cc.	
1	19 cc. ethyl ether	15.0	7.7
2	19 cc. benzene	18.0	9.2
3	19 cc. of a mixture of acetone and benzene (4 cc. of acetone and 15 cc. of benzene)	17.0	15.3
4	4 cc. ethyl alcohol and 15 cc. benzene	14.0	9.2
5	13.3 cc. methyl glycol plus 15 cc. benzene	14.0	33.6
6	8.6 cc. diethylene glycol monoethyl ether plus 15 cc. benzene	15.0	21.6

Ethyl ether and benzene are equally effective as oil solvents. The lower results obtained with ethyl ether can be attributed to the ether dissolved in the water retaining some of the oil. This solution of ether in the water is represented by the 3 cc. lower volume of the oil solvent in test No. 1 as compared with test No. 2. Calculating the 7.7 reading to a solvent volume of 18 ccs. will give a 9.2 reading for oil content which equals that of the benzene.

Tests Nos. 3, 5, 6 compared with test No. 2 show the increase of oil extracted by the addition of the water miscible substances.

Test No. 4 compared with the other tests where water miscible substances were used shows the necessity of using a substance which has some solvent action on oil. The solvent action of alcohol on oil is so slight that the alcohol is unable to dissolve the oil film adsorbed to the adsorbed water layer and therefore a mixed interfacial film is not produced. As a result the amount of oil obtained is the same as that obtained with benzene alone.

The high results of test No. 5 illustrate the effect of using a water miscible substance which dissolves organic material, producing a fluorescent effect, and their solution in the oil solvent, thereby giving a high oil result, which, however, is of value if all the samples are treated in the same manner. The following table shows the effect of using varying amounts of methyl glycol with 15 cc. of benzene on the oil obtained.

Treatment	Oil parts Per million
8 cc. methyl glycol	21.6
13 cc. methyl glycol	30.6
18 cc. methyl glycol	44.5

Based on the above, the following are the requirements for the oil solvent and the water miscible substance added for obtaining the greatest oil extraction. The oil solvent should be practically insoluble in water and the same should not be retained to any great amount in the water layer. The water miscible substance should have a small solvent action on the petroleum oil.

The oil solvent extract obtained as a result of the foregoing procedure will contain microscopic quantities of oil and these quantities will be practically unweighable. The Campbell Patent 2,227,438, previously referred to, discloses and claims one preferred method of quantitatively determining the oil content of such extracts but other methods may be employed and it is understood that the claims are not limited to any method except to exclude weighing operations, which operations can not be employed in any event, since the oil qauntities are too small to be weighed. The Campbell method subjects the extract to ultra-violet light to cause the oil content to fluoresce. The instrument producing the ultra-violet light may comprise any of the standard devices on the market which are equipped with very accurate means for measuring the fluorescence of the material subjected to ultra-violet light. Generally in such instruments the fluorescent light from the extract is passed through special filters to a photoelectric cell connected in circuit with a galvanometer whereby a current is caused to flow to the galvanometer proportional to the intensity of the fluorescent effect. The reading of the galvanometer can be converted into terms of oil by comparing the fluorescence produced by known amounts of crude oil dissolved in a similar solvent. These standard solutions of known concentration may range preferably from .001 milligram to 1 milligram. In this connection, it is only necessary to calibrate the instrument by testing the solutions wherein the petroleum oil concentration of each is known and following such calibration the amount of oil in an unknown extract may be readily determined.

Even though an incomplete extraction of the oil is obtained by the use of method No. 1, the results are of value if the same procedure is used on all samples compared. In the case of method No. 2, where the use of a water miscible substance such as methyl glycol, gives high oil results by reason of the solvent action of the methyl glycol on fluorscent producing materials other than petroleum oil, if the same procedure is used on all samples compared the results obtained are of value.

While we use standard solutions of petroleum oil to calibrate the galvanometer because the fluorescent effect with which we are concerned is that produced by the oil extracted from the samples, the galvanometer readings themselves can be used directly without converting them into terms of oil because the fluorescent effect produced by the oil is directly proportional to the oil contained in the extract subjected to the action of the ultra-violet light. Likewise, the galvanometer could be calibrated in terms of other fluorescent substances such as quinine sulphate and the variations in the fluorescence could be expressed in terms of this material. In any case, the variations in the intensity of the fluorescent light is due to variations in the oil content of the extract and hence of the sample being analyzed.

Where the quantity of the fine material produced by dispersing an earth sample is insufficient to obtain accurate results, the entire sam-

ple is extracted according to the methods described and the oil content of the extract determined. Because of the fact that there may be large variations in the surface area of particles composing different samples, the results obtained should be expressed in terms of oil per standard surface area for the purpose of comparison.

What is claimed is:

1. In a method of exploring for subterranean oil deposits, the step of treating an earth sample containing petroleum oil in practically unweighable quantities and in adsorbed relation to water contained in the earth sample, which includes an extraction process using a relatively water-insoluble oil solvent having a work of adhesion to water greater than the work of adhesion of petroleum oil to water, whereby as a result of the said extraction process the solvent will thus contain the adsorbed oil previously in the earth sample.

2. In a method of exploring for subterranean oil deposits, the step of treating a measured quantity of material containing petroleum oil in practically unweighable quantities and in adsorbed relation to water contained in the material, said material being selected from the group consisting of earth, drilling fluid and water, which includes an extraction process using a measured quantity of a relatively water-insoluble oil solvent having a work of adhesion to water greater than the work of adhesion of petroleum oil to water, whereby as a result of said extraction process the solvent will thus contain the adsorbed oil previously in the sample of material.

3. In a method of exploring for subterranean oil deposits, the step of treating an earth sample containing petroleum oil in practically unweighable quantities and in adsorbed relation to water contained in the earth sample, which includes an extraction process using a relatively water-insoluble oil solvent having a work of adhesion to water not less than thirty-six ergs per square centimeter at twenty-five degrees centigrade, whereby as a result of the said extraction process the solvent will thus contain the adsorbed oil previously in the earth sample.

4. In a method of exploring for subterranean oil deposits, the step of treating a measured quantity of material containing petroleum oil in practically unweighable quantities and in adsorbed relation to water contained in the material, said material being selected from the group consisting of earth, drilling fluid and water, which includes an extraction process using a measured quantity of a relatively water-insoluble oil solvent having a work of adhesion to water in excess of thirty-six ergs per square centimeter at twenty-five degrees centigrade, whereby as a result of said extraction process the solvent will thus contain the adsorbed oil previously in the sample of material.

5. In a method of exploring for subterranean oil deposits, the step of treating a measured quantity of material containing adsorbed petroleum oil in practically unweighable quantities and in adsorbed relation to water contained in the material, said material being selected from the group consisting of earth, drilling fluid and water, which includes an extraction process using a water miscible substance having a solvent action on petroleum oil together with a relatively water-insoluble oil solvent having a work of adhesion to water greater than the work of adhesion of petroleum oil to water, whereby as a result of the said extraction process the oil solvent will thus contain the oil previously in the sample of material.

6. In a method of exploring for subterranean oil deposits, the steps of treating an earth sample containing adsorbed petroleum oil in practically unweighable quantities, and in adsorbed relation to water contained in the earth sample, which includes adding a solution of a dispersing agent to said sample, and subjecting a measured quantity of the dispersed phase to an extraction process using a relatively water-insoluble oil solvent having a work of adhesion to water greater than the work of adhesion of petroleum oil to water, whereby as a result of the extraction process the oil solvent will thus contain the oil previously in the said dispersed phase of the sample.

7. In a method of exploring for subterranean oil deposits, the step of treating an earth sample containing adsorbed petroleum oil in practically unweighable quantities and in adsorbed relation to water contained in the earth sample, which includes adding a solution of a dispersing agent to said sample, and subjecting a measured quantity of the dispersed phase to an extraction process using a relatively water-insoluble oil solvent having a work of adhesion to water greater than the work of adhesion of petroleum oil to water together with a water miscible substance having a solvent action on petroleum oil, whereby as a result of said extraction process the oil solvent will thus contain the oil previously in the dispersed phase of the sample.

8. In a method of exploring for subterranean oil deposits, the improvement in the analysis of earth samples to quantitatively determine their content of petroleum oil in adsorbed relation to water, which consists in subjecting the samples to treatment without preliminary drying, said treatment including the step of extracting a measured quantity of each sample by using benzene as the oil solvent, together with a water miscible substance having a solvent action on petroleum oil, whereby the said benzene will contain the oil previously in the sample.

9. In a method of exploring for subterranean oil deposits, the improvement in the analysis of earth samples to quantitatively determine their content of petroleum oil in adsorbed relation to water, which consists in subjecting the samples to treatment without preliminary drying, said treatment including the step of extracting a measured quantity of each sample by using benzene as the oil solvent, to which has been added acetone to facilitate the extraction process, whereby the benzene will contain the oil previously in the sample.

10. In a method of exploring for subterranean oil deposits, the improvement in the analysis of samples of material from the earth to quantitatively determine their content of petroleum oil in adsorbed relation to water, which consists in subjecting the samples to treatment without preliminary drying, said treatment including the step of adding a solution of a dispersing agent to a measured quantity of each sample, subjecting a portion of the dispersed phase to an extraction process using a relatively water-insoluble oil solvent having a work of adhesion to water greater than the work of adhesion of petroleum oil to water, and adding a water miscible liquid also to said portion of the dispersed phase, said water miscible liquid being characterized by an ability to facilitate the solvent action of the oil solvent.

11. In a method of exploring for subterranean oil deposits, the improvement in the analysis of samples of material from the earth to quantitatively determine their content of petroleum oil in adsorbed relation to water, which consists in subjecting the samples to treatment without preliminary drying, said treatment including the step of adding a solution of sodium pyrophosphate as a dispersing agent to a measured quantity of each sample, subjecting a portion of the dispersed phase to an extraction process using a relatively water-insoluble oil solvent having a work of adhesion to water greater than the work of adhesion of petroleum oil to water, and adding a water miscible liquid also to said portion of the dispersed phase, said water miscible liquid being characterized by an ability to facilitate the solvent action of said oil solvent.

12. In the treatment of earth material to extract adsorbed petroleum oil which is present in practically unweighable amounts and in adsorbed relation to water, the steps including the preparation of a measured sample of the material, adding a measured quantity of an oil solvent to the said sample to extract the adsorbed oil therefrom, said oil solvent being relatively water-insoluble and having a work of adhesion to water greater than the work of adhesion of petroleum oil to water, agitating the mixture, and then effecting a separation of the oil solvent from the remainder of the mixture.

13. In the treatment of earth material to extract adsorbed petroleum oil which is present in practically unweighable amounts and in adsorbed relation to water, the steps including the preparation of a measured sample of the material, adding a measured quantity of an oil solvent to the said sample to extract the adsorbed oil therefrom, said oil solvent being relatively water-insoluble and having a work of adhesion to water in excess of thirty-six ergs per square centimeter at twenty-five degrees centigrade, agitating the mixture, and then effecting a separation of the oil solvent from the remainder of the mixture.

14. In the treatment of earth material without the necessity of preliminary drying to extract adsorbed petroleum oil which is present in practically unweighable amounts and in adsorbed relation to water, the steps including the preparation of a measured sample of the material, adding a measured quantity of an oil solvent to the said sample to extract the adsorbed oil therefrom, said oil solvent being relatively water insoluble and having a work of adhesion to water greater than the work of adhesion of petroleum oil to water, also adding a water miscible substance to the sample characterized by an ability to facilitate the solvent action of the oil solvent, agitating the mixture, and then effecting a separation of the oil solvent from the remainder of the mixture.

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