April 27, 1965 A. F. GULBRANDSEN 3,181,058

METHOD AND APPARATUS FOR DETERMINATION OF AMOUNT OF SALT IN HYDROCARBON OIL

Filed July 5, 1963 3 Sheets-Sheet 1

Fig. 1

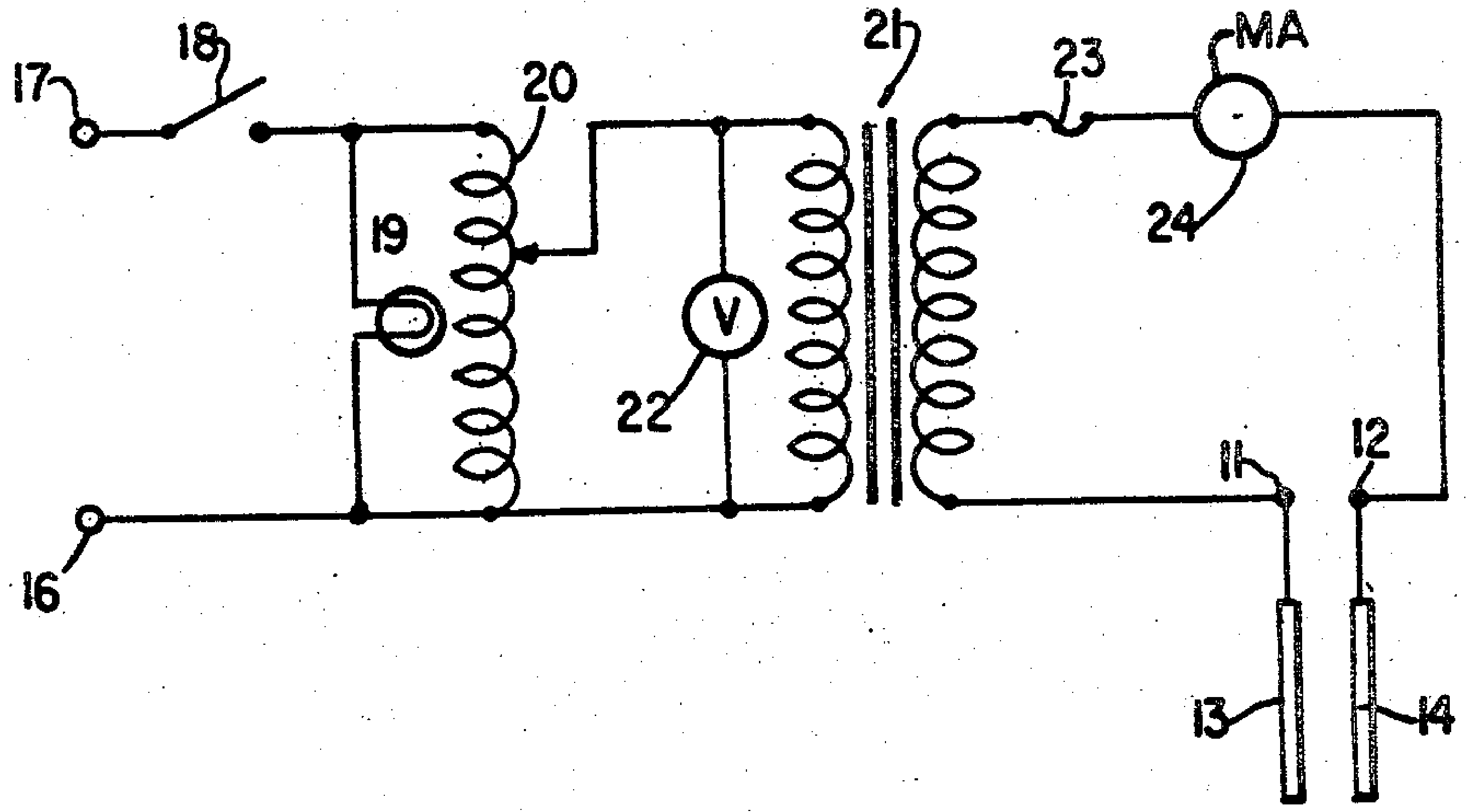
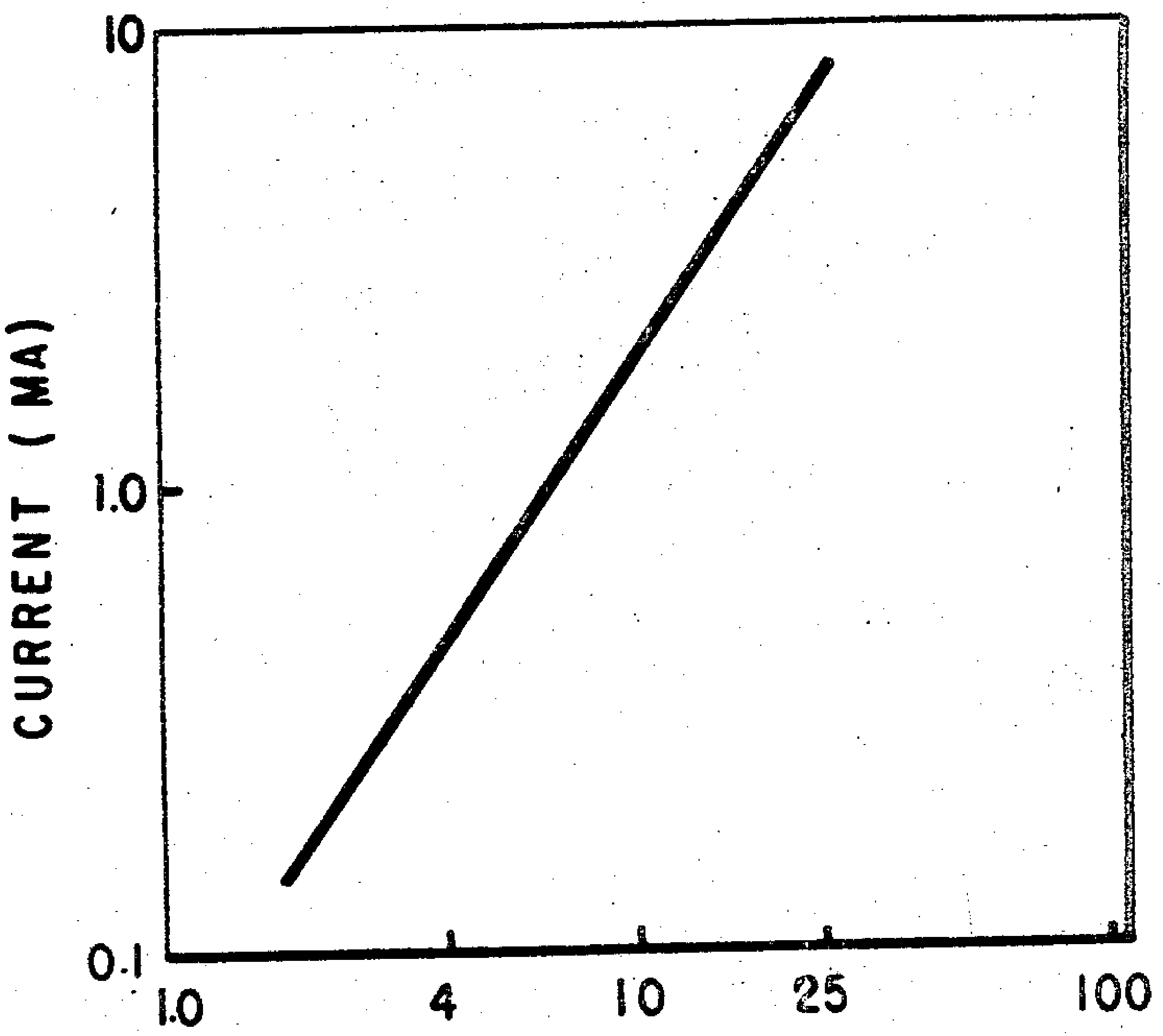


Fig. 2



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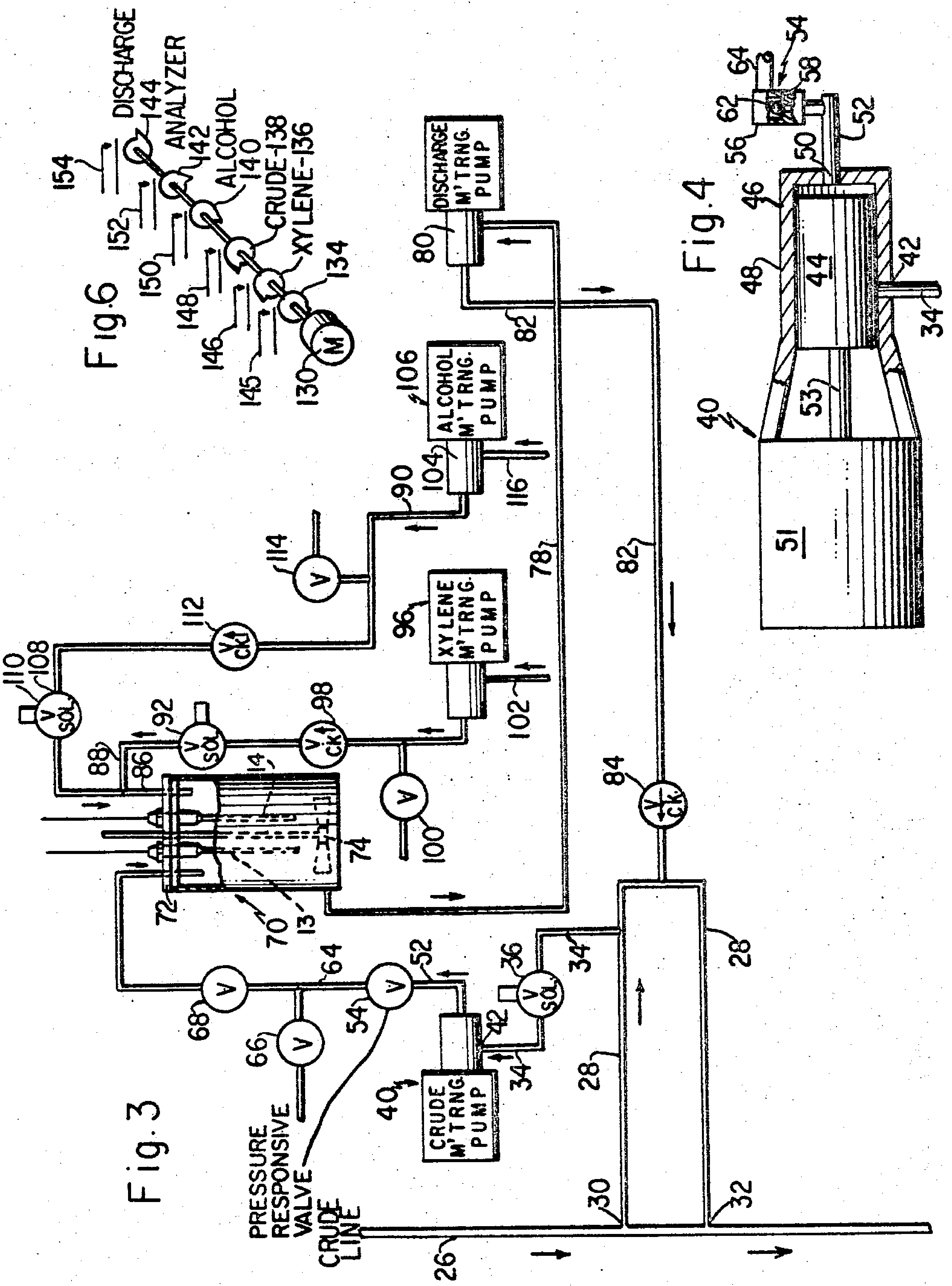

Fig.6

Fig.4

Fig.3

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METHOD AND APPARATUS FOR DETERMINATION OF AMOUNT OF SALT IN HYDROCARBON OIL

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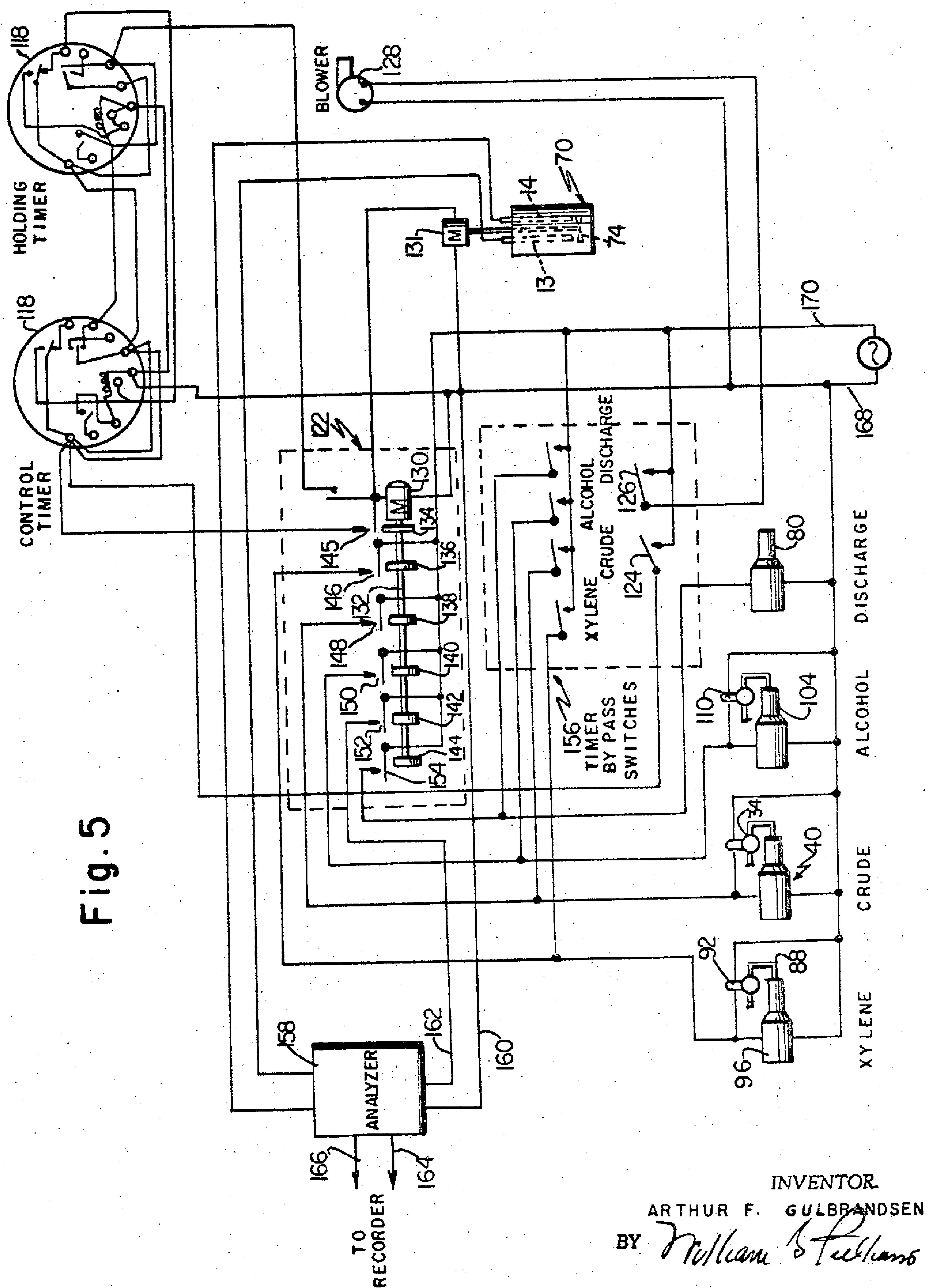

Fig. 5

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United States Patent Office

3,181,058
Patented Apr. 27, 1965

3,181,058

METHOD AND APPARATUS FOR DETERMINATION OF AMOUNT OF SALT IN HYDROCARBON OIL

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Filed July 5, 1963, Ser. No. 294,217
14 Claims. (Cl. 324—30)

This application is a continuation-in-part of my copending application Serial Number 148,137, filed on October 27, 1961, now abandoned.

This invention relates to the treatment of hydrocarbon oils and more particularly to apparatus and a method for the analysis of crude oil to determine the amount of salts present in the crude oil.

All crude oils, when produced, contain various amounts of emulsified salt solutions. Treatment in the field usually reduces the amount of such emulsion very materially but crude oils delivered to refineries still contain appreciable quantities of salts. In some instances the crude may still contain in excess of 100 lbs. of such salts per 1,000 barrels of oil. The composition of the salts in crude oils varies considerably but the salts present usually consist largely of the chlorides of sodium, calcium and magnesium with smaller amounts of sulfate and other anions. In the refinery the salt present in the crude oil tends to be deposited in heat exchanger tubes, thereby fouling the tubes and causing expensive shutdowns for cleaning. In addition, when such crude oil is heated, hydrolysis of the alkaline earth chlorides present liberates hydrochloric acid which corrodes vapor lines and condenser surfaces. For these reasons, it is important that the salt content of crude oil be reduced to the lowest practical limit prior to refining. In practice, the salt content of crude oils is frequently reduced to 3 or 4 lbs. per 1,000 barrels of oil or less.

The usual method for reducing the salt content of crude oil is by means of electrical precipitation. In order to know the most effective setting of the electrical instruments that control the desalting operation, it is necessary to know the salt content in the effluent crude oil coming from the desalting equipment. While there is no completely standard method for analysis for the salt content of crude oil, there are numerous methods in use in the industry. While not entirely similar, these methods are all alike in principle. In these methods of analysis a sample of the crude oil to be tested is thoroughly mixed or shaken with hot water to dissolve the salts. The aqueous solution is then separated and the salts present in the aqueous solution are determined by suitable means such as by titrating with standard silver nitrate solution. Due to the formation of emulsions, a number of hours may elapse before the water layer has separated completely enough so that the analysis can be completed. During this time the desalting equipment may or may not be functioning properly. Also, the results of such tests for salt content are frequently accurate only to about plus or minus 5% of the salt present.

It is an object of the present invention to provide an improved method and apparatus for determining the salt content of hydrocarbon oil by which the analysis may be completed in a very short length of time and with a high degree of accuracy.

It is another object of this invention to provide a method and apparatus for the determination of salt in hydrocarbon oil for refinery operations in the form of automatic continuous or intermittent salt determination in a flowing stream of oil and, where desired, a continuous or intermittent recordation of the salt content of that oil.

In accordance with a preferred embodiment of the present invention a sample of the crude oil to be analyzed for salt contents is first mixed with a suitable quantity of a polar organic solvent to form a homogeneous, single phase solution. If the crude oil contains appreciable quantities of asphaltic material, it is preferred to use a strong non-polar organic solvent in addition to the polar solvent to insure that the asphaltic material is dissolved in the solution and is not precipitated by the addition of the polar solvent. Generally the mixture of crude with the polar organic solvent or the mixture of crude, polar organic solvent and the non-polar organic solvent must be thoroughly mixed to form a homogeneous mixture. When the crude contains appreciable quantities of asphaltic material it is preferred to first mix the crude with the non-polar solvent to form a homogeneous mixture and then to add the polar solvent to this mixture and form the final mixture to be tested. If the polar organic solvent is added to crude containing appreciable quantities of asphaltic material prior to the mixture of this crude with a non-polar organic solvent, a precipitate forms which deposits on the equipment and which often causes erroneous test readings. The resulting single phase solution is then contacted with spaced electrodes maintained at a known potential with alternating current and the conductivity of the solution is measured by measuring the flow of alternating current between the electrodes.

For a better understanding of the invention reference should be had to the accompanying drawings wherein identical numerals refer to identical parts and in which

FIGURE 1 is a diagrammatic illustration of apparatus suitable for carrying out a preferred embodiment of the invention;

FIGURE 2 is a graph showing the relationship between salt content of crude oil and current passing between electrodes when practicing a preferred embodiment of the invention with the apparatus shown in FIGURE 1;

FIGURE 3 is a digrammatic representation of preferred apparatus for use with a method for the automatic intermittent analysis of a flowing stream of crude in a refinery;

FIGURE 4 is a diagrammatic representation of a positive displacement metering pump and some of its associated parts which is used for metering crude;

FIGURE 5 is a diagrammatic representation of an electrical circuit and associated parts which can be used with the apparatus of FIGURE 3; and

FIGURE 6 is a diagrammatic representation of the sequence timer which can be used in the electrical circuit of FIGURE 5.

Referring to FIGURE 1, suitable apparatus is shown for maintaining a constant alternating current potential at terminals **11** and **12** of electrodes **13** and **14**. While any suitable means for providing a suitable alternating current potential across these electrodes may be used, the apparatus shown and described in FIGURE 1 has been found convenient for this purpose. As shown in FIGURE 1, the apparatus may include terminals **16** and **17** adapted to be connected to a suitable source of alternating current such as ordinary 115 volt house current. A switch **18** may be provided for shutting off the A.C. potential without necessity for disconnecting the terminals **16** and **17** and a pilot light **19** may be provided to indicate when the apparatus is connected and ready for use. In order to insure a constant alternating current potential at the electrodes **13** and **14**, an adjustable auto transformer **20** may be provided to control the voltage supplied to the input side of a transformer **21**. A volt meter **22** is preferably provided to measure the voltage supplied to the input of the transformer **21**. While not essential, the transformer **21** may be used to increase the voltage across the electrodes **13** and **14** above that available at the terminals **16** and **17**. As indicated in FIGURE 1, the output side of the transformer **21** is connected to the terminals **11** and **12** of the electrodes **13** and **14** to supply a constant alternating current potential thereto. A fuse **23** may be used to insure against overloading and suitable means such as a milliammeter **24** are provided for measuring the flow of current between the electrodes **13** and **14**.

In the practice of the present invention a mixture of crude oil and solvent prepared as described below is contacted with electrodes **13** and **14**. The current which passes between the electrodes at a given voltage is measured by the milliammeter **24** to provide an indication of the amount of salts present in the crude oil. It has been found that the conductivity of solutions of crude oil and solvent containing salts does not appear to depend upon the particular salt present or the relative proportions of several of the various salts commonly found in crude oil. It has, therefore, been found possible by testing a number of crude oil samples of known salt content, to make up a graph, such as the one shown in FIG. 2, showing the current readings obtained at a given voltage with crude oils containing varying amounts of salt. Such a graph may then be used as a reference curve to determine the amount of salt present in an unknown solution. Thus, once the apparatus has been assembled and reference graphs such as that shown in FIG. 2 obtained, a sample of crude oil of unknown salt content may be analyzed extremely rapidly merely by contacting a solution of such crude oil and solvent with the electrodes **13** and **14**, measuring the current passing between the electrodes and determining from the reference graph the salt content corresponding to the measured current flow. It is, of course, necessary that the same proportions of the same solvent and the same test conditions be used in preparing the reference graph and in analyzing the unknown crude oil samples.

The apparatus in FIG. 3 is particularly suited for the automatic intermittent analysis of salt in crude in refinery operations, particularly in determining the salt content of crude which has passed through a desalter. A pipeline **26** carries a flowing stream of crude at 220 p.s.i.g. A smaller diameter conduit or line **28** is tapped into pipeline **26** so that crude constantly circulates from the inlet **30** of line **28** to outlet **32** of said conduit. Intermediate the ends **30** and **32** of conduit **28** another conduit **34** is tapped into line **28**. A solenoid valve **36** is interposed in conduit **34**. Valve **36** permits crude to enter the electrical metering pump **40** through inlet **42**. Pump **40** is a Milton-Roy pump, Model MDI–23–45 of 2.25 g.p.h. capacity.

As shown in FIG. 4 pump **40** comprises a piston **44**, reciprocable in a cylinder **46** formed within a body **48**, and rod **50** connected to an electrical motor **51**. The body **48** has an outlet passage **50** which communicates with one end of conduit **52** having a pressure responsive valve **54** at its other end. Pressure responsive valve **54** comprises a housing **56** a valve seat **58**, and a ball urged against the seat **58** by spring **62**. Valve **54** permits liquid to flow therethrough when a pressure of 250 p.s.i.g. is imparted to the crude by pump **40**. Valve **54** is thus in a normally closed position but is actuatable to permit oil to flow from the pump to the sample receiver when the pressure in conduit **52** between the pump outlet and the valve **54** is greater than the pressure in the pipe line **26**, conduit **28** and conduit **34**. Valve **54** communicates with one end of conduit **64** which has a manually operated by-pass valve **66** and a manually operated valve **68** in the line. Normally valve **66** is closed and valve **68** is open. The other end of conduit **64** communicates with and supplies measured quantities of oil to sample receiver **70** which is fitted with plate **72**, stirrer **74** and electrodes **13** and **14**.

The bottom of the sample receiver **70** communicates with one end of conduit **78**, so that liquid contents thereof can be drained, which in turn communicates with the inlet of electrical metering pump and motor **80**. Metering pump and motor **80**, as with the other metering pumps and motors of the drawings, are substantially identical to that of electrical metering pump and motor **40**. Generally, means are provided such as a U-bend in conduit **78** so as to prevent appreciable quantities of oil from flowing from the sample receiver into the conduit **78** unless the pump **80** is activated. One end of conduit **82** communicates with the outlet of pump **80** while the other end thereof communicates with the conduit **28** downstream of the connection of conduit **28** with conduit **34**. A one way check valve **84** prevents the flow of crude from conduit **28** into conduit **82**. Conduit **86** communicates with sample receiver or cell **70** and carries a substantially anhydrous xylene from one end of conduit **88** and a mixture of substantially anhydrous alcohol from one end of conduit **90**. Pipeline **88** has a solenoid valve **92** interposed therein. The other end of pipeline **88** is operatively connected to the outlet side of electrical pump and motor **96**. Intermediate solenoid valve **92** and pump **96** is a one way check valve **98** and relief valve **100**. The inlet side of pump **96** communicates with one end of pipeline **102** which supplies xylene thereto from a suitable container which is not shown. One end of pipeline **90** communicates with the pump **104** which is operatively connected to electric motor **106**. Intermediate the ends of pipeline **90** is a valve **108** controlled by solenoid **110**, a one way check valve **112** for preventing the flow of alcohol back into pump **104** and a pressure relief valve **114**. Communicating with the inlet side of pump **104** is one end of pipeline **116** while the other end of this pipeline communicates with a source of a mixture of alcohols not shown. The mixture of alcohols contains 37 volume percent methanol and 63 volume percent n-butanol.

The operation of the apparatus of FIGS. 3 and 4 is controlled by the electrical circuits shown in FIG. 5. Three timing mechanisms are interposed in the electrical circuit. All three of these timers are simply referred to herein collectively as a program timer. The individual timers are a control timer **118**, a holding timer **120** and a sequence timer **122**. Timers **118** and **120** are well known timers and the combination unit of timers **118** and **120** is commercially available, e.g. Cramer-Type 742 timer. The sequence timer **122** is also a commercially available timer. One such timer is a Cramer-Type 521, 8 pole timer which makes one revolution in three minutes. The electrical circuit of FIG. 5 is closed by manually operated timer switch **124** which is normally in the closed position. A manually operated switch **126** is also provided for energizing blower **128** to provide air circulation about the apparatus.

Sequence timer **122** comprises an electric motor **130**. Keyed into shaft **130** are cams **134**, **136**, **138**, **140**, **142** and **144**. On revolution of the shaft **130** cam **134** closes electrical contacts **144** which energizes motor **130** and stirrer motor **131**. Cam **134** keeps contacts **144** closed during the entire analysis cycle which lasts for 3 minutes during which time the remaining cams actuate their corresponding electrical contacts for predetermined periods of time. Cam **136** closes electrical contacts **146** which actuate xylene pump **96** and open solenoid valve **92** for 40 seconds to meter 60 cc. of xylene into sample receiver **70**. Cam **138** closes electrical contacts **148** which actuate crude pump **40** and open solenoid valve **36** for 10 seconds to meter 10 cc. of crude into sample receiver **70**. Contacts **148** are closed prior to transferring all the xylene to receiver **70**. Cam **140** closes electrical contacts **150** which actuate the alcohol pump **104** and open solenoid valve **108** for 35 seconds to meter 50 cc. of the alcohol mixture to sample receiver **70**. Cam **142** closes electrical contacts **152** after the alcohol is thoroughly stirred in receiver **70**. Contacts **152** energize the analyzer **158** and its associated electrodes **13** and **14** for 15 seconds. Cam **144** closes electrical contacts **154** which actuate discharge pump **80** after the analyzer is turned off. The discharge pump operates for the remainder of the 3 minute analysis cycle. It drains receiver **70** and pumps the analyzed liquid into conduit **28.**

The circuit also contains momentary contact switches **156** to actuate manually when desirable, each of the pumps and solenoids for xylene, crude, alcohol and the discharge pump. The analyzer **158** can be identical to that shown in FIG. 1 except that the power source of the analyzer is through wires **160** and **162** and the ammeter **24** can be eliminated or its terminals operatively connected by wiring **164** and **166** to a recorder which is not shown.

In the automatic intermittent operation of the apparatus shown in FIGS. 3–6, a constant supply of 60 cycle 117 volt alternating current is provided for the electrical circuit by wires **168** and **170** through source **169**. The timer switch **124** is closed and this starts the control timer **118.** The control timer can be set for any time between 0 and 60 minutes. In the preceding description it was set for 15 minutes. When the control timer **118** reaches a preset point, e.g. 15 minutes, it energizes holding timer **120.** The control timer **118** then goes to its reset position to start the cycle again, e.g. for 15 minutes. The holding timer **120** bypasses sequence timer motor switch **144** but energizes motor **130** until the cam actuated motor switch **144** in sequence timer **122** is closed. On closing of contacts **144** holding timer **120** goes to its reset position and sequence timer motor **130** is controlled by cam **134** and contacts **144.**

In determining the salt content of crude oil in accordance with the present invention the mixture of diluent or diluents and crude oil should be a single phase, homogeneous mixture in which the salt present in the crude gives the mixture sufficient conductivity to be capable of measurement as described above. The salt in crude oils to be measured in accordance with the invention is usually present in the form of a water emulsion which is present in very small amounts and does not form a continuous phase. Direct measurement of the conductivity of such crude oil samples is generally impractical or impossible. While the quantity of polar solvent (or diluent) to be added may vary over extremely wide ranges and the amount to be used is almost entirely within the choice of the operator, it has been found convenient in many instances to use between about 1 and about 100 volumes of polar solvent per volume of crude oil. Mixing or shaking the crude oil with such solvent forms a homogeneous single phase solution or mixture which may then be tested for salt content by contacting it with a pair of spaced electrodes such as the electrodes **13** and **14** described above. Organic polar solvents suitable for this purpose include but are not limited to such solvents as alcohols and ketones, e.g. methyl alcohol, n-butyl alcohol, acetone, ethyl alcohol, propylene glycol, etc. While any suitable organic polar solvent or mixtures thereof may be used, alcohols containing from 1 to about 6 carbon atoms and particularly alkanols, have been found especially useful for this purpose. Preferably the polar solvent is a mixture of alkanols such as methanol and n-butanol. In one preferred embodiment the volume of methanol and n-butanol is from 3 to 7 times the volume of crude sample wherein the volume of methanol in the alcohol mixture is from about 0.3 to 2 parts methanol per part of n-butanol; also, in such a combination it is preferred that the non-polar solvent, e.g. xylene, is from about 3 to 7 times more than the volume of crude.

Where the crude oil to be tested contains asphaltic material (considered herein as being hydrocarbon material which is not soluble in pentane), strong non-polar organic solvents are preferably used in addition to the polar solvent in order to prevent precipitation of asphaltenes or other asphaltic material. For present purposes, strong organic solvents may be considered those which are capable of dissolving asphaltic material. Such solvents include, but are not limited to benzene, toluene, xylene, carbon tetrachloride, diethyl ether, ethyl acetate, etc., or combinations of suitable solvents. Of such solvents, aromatic hydrocarbon solvents have been found especially suitable. The use of such strong non-polar organic solvents is preferred whenever the crude oil to be tested contains asphaltic material. Such asphaltic material is usually present in crude oil having gravities lower than about 30° API. In accordance with standard practice in the petroleum industry, degrees API are measured in accordance with the standards established by the American Institute. API gravity may be determined in accordance with test method D287–55 as described in "ASTM Standards on Petroleum Products and Lubricants," volume I, 1962, published by the American Society for Testing Methods and Materials. In devising standardized test procedures in accordance with the invention, it is preferred to include suitable quantities of such strong non-polar organic solvents so that use of the standardized test and reference graph will not be limited to crude oils which do not contain asphaltic material but can be used on most commonly encountered crude oils.

When non-polar strong organic solvents or diluents of the type described above are used they may be used in suitable quantities such as between about 1 and about 100 volumes based on the amount of crude oil present. As in the case of the polar solvents, however, the practice of the invention is not limited to the use of solvents in these proportions or concentrations and, especially when the salt content of the crude is relatively high, it may be desirable to use considerably greater amounts of solvents in order to keep the current readings obtained across the across the electrodes fairly low. In this respect, concentrations of solvents yielding relatively low current readings are preferred since, as can be seen from FIGURE 2, the method of analysis described herein is more accurate under such circumstances. Also, of course, with a given equipment setup it may be desirable to bring all of the test data within the range of a single scale milliammeter without the necessity for providing a multi-scale instrument or switching scales.

While it is preferred in practicing the present invention to keep the water content of the solution being tested at relatively low values, such as below about 0.5 volume percent, the presence of greater quantities of water does not adversely affect the analysis except that, as in the case of solvents, the proportions and quantities of water must be kept constant in order to obtain reliable comparative data. Generally speaking relatively larger quantities of water increase the conductivity of the solution and excessive amounts of water in any given solution make it difficult or impossible to achieve a single phase homogeneous solution and in general lead to the same difficulties experienced with oil-water emulsions in the practice of previously known methods of analysis for the presence of salts in crude oil.

It is especially important in practicing the present invention that the electrodes be maintained at the desired potential with alternating current. The use of direct current has been found to be entirely unsatisfactory for this purpose due to deposition of constituents of the crude oil on one or more of the electrodes. These deposits build up quite rapidly and have the effect of completely destroying the validity of the data obtained by reducing the apparent conductivity and current readings by unknown factors which vary according to the rapidity and type of deposits built up. While it is essential that alternating current be used, the voltage which is employed may as mentioned above vary over extremely wide ranges at the discretion of the operator. For instance, the use of voltages at the electrodes within the range of between about 50 and about 500 volts is satisfactory.

The following examples will illustrate the application of one preferred embodiment of the invention using apparatus of the type described above and shown in FIGURE 1.

EXAMPLE 1

In order to establish a reference curve for further evaluation of unknown samples, various samples of crude oil and lubricating oil containing known amounts and proportions of various salts were analyzed in accordance with the present invention. In these tests each sample contained salt in the amounts and proportions indicated in Table I below. Milliammeter readings obtained for these tests are also shown in Table I and the results obtained are shown graphically in FIGURE 2.

In these tests each 10 milliliter sample was dissolved by mixing in 90 milliliters of a volumetric mixture of 40% xylene, 38% N-butyl alcohol and 22% methyl alcohol (all materials anhydrous) to form a single phase, homogeneous solution and placed in an ASTM dissolved gum test beaker. The electrodes were placed in the beaker and the milliammeter reading was noted at a primary voltage (25 volts) corresponding to a voltage of 125 volts across the electrodes. The electrodes for these tests were stainless steel plates measuring 1 inch by 2 inches by $\frac{1}{16}$ inch and were spaced $\frac{1}{4}$ inch apart.

Using the results shown in Table I below a reference curve was plotted and is shown as FIGURE 2. Due to the number of data points used in plotting the curve of FIGURE 2 they are not individually reproduced but all were grouped extremely close to the resulting curve, thus indicating extremely reproducible results.

Table I

Composition of salts, wt. percent	Oil	Amount of salts (lbs./1,000 bbl. of oil)	Current (Mo.)
Sodium chloride, 33.3 Calcium chloride, 33.3 Magnesium chloride, 33.3	Lubricating oil	4	0.42
		10	1.85
		25	6.3
		50	(1)
Sodium chloride, 50 Calcium chloride, 25 Magnesium chloride, 25	Lubricating oil	4	0.45
		10	1.9
		25	6.8
		50	(1)
Sodium chloride, 33 Calcium chloride, 33 Magnesium chloride, 33	Crude oil	4	0.35
		10	1.86
		25	7.3
		50	(1)
Sodium chloride, 50 Calcium chloride, 25 Magnesium chloride, 25	Crude oil	4	0.46
		10	1.86
		25	7.8
		50	(1)

[1] Off scale.

The following examples are cited to demonstrate the accuracy of results obtainable using the method of the present invention in conjunction with a reference curve of the type shown in FIGURE 2. All of the following tests described below were made with the same apparatus used in Example 1 and the same voltage was maintained across the electrodes.

EXAMPLE 2

Ten milliliters of a mid-continent crude oil, when dissolved in 90 milliliters of the xylene-alcohol solvent described in Example 1, gave a current reading of 7.4 milliamperes when tested as described in Example 1. From the reference curve shown in FIGURE 2, this is equivalent to a salt content of 25 lbs. per 1,000 barrels of oil. A salt content of 25 lbs. per 1,000 barrels of this oil was determined by a conventional extraction and titration analysis.

EXAMPLE 3

Ten milliliters of a Canadian crude oil, the effluent from an electrical desalter, when dissolved in 90 milliliters of the xylene-alcohol solvent of Example 1 under the test conditions of Example 1, gave a reading of 0.38 milliampere current flow across the electrodes. From the curve of FIGURE 2, this is equivalent to 3.5 lbs. of salt per 1,000 barrels of oil. A salt content of 4 lbs.

per 1,000 barrels of oil was determined by conventional analysis.

EXAMPLE 4

Ten milliliters of a mid-continent crude oil, when dissolved in 90 milliliters of the xylene-alcohol solvent of Example 1 under the test conditions of Example 1, gave a reading of 4.0 milliamperes. From the reference curve of FIGURE 2, this would indicate the presence of 16.5 lbs. of salt per 1,000 barrels of oil. A conventional extraction analysis indicated 17 lbs. of salt per 1,000 barrels of oil.

EXAMPLE 5

Five milliliters of a Gulf Coast crude oil were diluted with 5 milliliters of xylene and the mixture dissolved in 90 milliliters of the xylene-alcohol solvent of Example 1. A reading of 5.6 milliamperes under the test conditions of Example 1 was obtained. This was equivalent to 21 lbs. of salt per 1,000 barrels of oil as indicated by the reference curve of FIGURE 2. However, since in this example only 5 milliliters of sample crude oil was used, the result was multiplied by 2 to obtain the equivalent of a 10 milliliter sample test. The value of 42 lbs. of salt per 1,000 barrels of oil thus obtained compares with a value of 37 lbs. per 1,000 barrels of oil obtained by conventional extraction analysis.

EXAMPLE 6

50 milliliters of Panuco crude oil was diluted with 50 milliliters of xylene and, as in the other examples cited, shaken to dissolve the crude and obtain a single phase homogeneous solution. 3 milliliters of the diluted solution (equivalent to 1.5 milliliters of the original crude oil) was further diluted with 7 milliliters of xylene. This mixture, when dissolved in 90 milliliters of the xylene-alcohol solvent of Example 1, gave a reading of 2.3 milliamperes under the test conditions of Example 1. According to the reference curve of FIGURE 2, this is equivalent to 11.5 lbs. of salt per 1,000 barrels of oil. However, the standard of FIGURE 2 was based on a 10 milliliter sample so that the value of 11.5 must be multiplied by 6.67 (10 divided by 1.5) to obtain an indicated value of 77 lbs. of salt per 1,000 barrels of oil. A conventional extraction analysis of this crude oil indicated a salt content of 82 lbs. per 1,000 barrels of oil.

While the invention has been described above with respect to certain preferred embodiments thereof, it will be understood by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention and all such changes and modifications are intended to be covered by the appended claims. Illustratively a second crude metering pump and its associated parts can be employed with the apparatus in FIGS. 3–6 in order to determine salt content of crude going into a desalter. Also, appropriate conduits and valves can be attached to conduit 34 to drain crude therefrom prior to the analysis cycle in order to obtain a more representative sample of the crude in line 26.

I claim:

1. A method for determining the amount of salt in hydrocarbon oil containing the same which comprises mixing said oil with a polar organic solvent to form a homogeneous mixture, contacting the resulting mixture with a pair of spaced electrodes maintained at alternating current potential and measuring the flow of current between said electrodes.

2. The method for determining the amount of chloride salts in crude oil containing the same and substantially free of asphaltic material which comprises mixing said crude oil with a polar organic solvent to form a homogeneous single phase solution, contacting the resulting solution with a pair of spaced electrodes maintained at known alternating current potential and measuring the flow of current between said electrodes.

3. The method for determining the amount of salt in crude oil containing the same and which contains asphaltic material which comprises mixing a sample of said crude oil with at least one polar organic solvent and at least one strong non-polar organic solvent to form a homogeneous solution, contacting the resulting solution with a pair of spaced electrodes maintained at known alternating current potential and measuring the flow of alternating current between said electrodes.

4. The method of claim 3 in which the salt is predominately a chloride, the polar and non-polar organic solvents is each present in amounts between 1 and 100 times the amount of crude oil present, the polar organic solvent is a mixture of alkanols having from 1 to 6 carbon atoms and wherein the crude is mixed with the non-polar organic solvent prior to contact with the polar organic solvent.

5. The method for determining the amount of chloride salts in crude oil containing the same and which contains asphaltic material and has an API gravity less than about 30° as measured by ASTM Method D287–55 which comprises mixing a predetermined quantity of at least one strong non-polar organic solvent to form a homogeneous, single phase solution containing less than about 0.5 volume percent water, said sample being mixed with the non-polar organic solvent prior to mixing with the polar organic solvent, contacting the resulting solution with a pair of spaced electrodes maintained at known alternating current potential and measuring the flow of alternating current between said electrodes as a measure of the concentration of the chloride salt.

6. The method of claim 5 wherein the non-polar organic solvent is xylene and the polar organic solvent is a mixture of methanol and n-butanol.

7. The method for analyzing a crude oil sample to determine the chloride salt content thereof which comprises the following steps:

(1) Subjecting each of a number of crude oil samples containing known amounts of salts to an analysis including the steps of:
   (*a*) Mixing said sample with between about 1 and about 100 volumes of polar organic solvent and between about 1 and about 100 volumes of strong non-polar organic solvent based on volume of crude oil to form a homogeneous solution;
   (*b*) Contacting said solution with a pair of spaced electrodes maintained at known alternating current potential;
   (*c*) Measuring the flow of alternating current between said electrodes;

(2) Analyzing said sample of crude oil of unknown salt content according to steps *a*, *b* and *c* above under the same conditions used in analyzing the samples of known salt content; and

(3) Correlating the flow of current through said solution of crude oil of unknown salt content with the flow of current through the solutions of crude oil samples of known salt content to derive information indicative of the amounts of chloride salts present in the crude oil sample of unknown salt content.

8. A process for determining the concentration of salt in a flowing stream of crude under pressure from a desalter, said crude containing asphaltic material, having an API gravity of less than about 30° and containing less than about 0.5% by volume of water, which comprises passing a portion of the crude stream through a conduit, increasing the pressure on the crude in said conduit above that in the remaining stream of crude, metering a predetermined volume of a crude sample in the conduit, decreasing the pressure on the sample and passing it into a sample receiver, mixing a predetermined volume of substantially anhydrous xylene with the sample in the sample receiver to form a homogeneous mixture, the volume of xylene being from about 2 to 6 times greater than the volume of crude, mixing a predetermined volume of a substantially anhydrous mixture of methanol and n-butanol with the mixture of crude and xylene in the sample receiver to form a homogeneous liquid mixture thereof, the volume of the mixture of methanol and butanol being from about 3 to 7 times the volume of crude and wherein the volume of methanol in said methanol and butanol mixture is from about 0.3 to 2 parts of methanol per part of n-butanol, contacting the mixture of crude, xylene, methanol and n-butanol with a pair of spaced electrodes maintained at alternating current potential, measuring the flow of alternating current between the electrodes as a measure of salt concentration, drawing the liquid mixture from the sample receiver through a conduit, increasing the pressure of the liquid mixture above that in the flowing stream of crude and finally injecting the liquid mixture into said flowing stream on the downstream side from which the crude sample was obtained.

9. Analysis apparatus for determining salt content of hydrocarbon oil flowing through a pipeline at elevated pressures which comprises a sample receiver, means for metering a sample of predetermined volume of said hydrocarbon into said sample receiver, said metering means comprising a metering pump, a conduit having valved means therein for receiving oil at high pressures from the pipeline and operatively connected to the pump inlet, a second conduit positioned to conduct oil from the pump outlet to the sample receiver and a normally closed pressure responsive valve in said second conduit, means for metering and mixing with said sample a predetermined volume of a diluent liquid, a pair of spaced electrodes adapted for immersion in said sample and diluent mixture in said sample receiver, means for measuring electrical conductivity of said mixture between the spaced electrodes and means for draining the mixture of sample and diluent from said sample receiver.

10. Apparatus for determining the amount of salt in hydrocarbon oil containing the same comprising a positive displacement pump, first conduit means and a normally closed valve for controlling the flow of oil from a source of oil into the pump inlet, a sample receiver, second conduit means for conducting oil from the pump outlet to said sample receiver, a normally closed pressure responsive valve in said second conduit means actuatable at a pressure above that in said first conduit to permit a predetermined quantity of oil from the pump to flow into said sample receiver, first metering means for metering and mixing a predetermined quantity of a first diluent for the oil in the sample receiver, second metering means for metering and mixing a predetermined quantity of a second diluent with the oil and first diluent in the sample receiver, a pair of spaced electrodes in said sample receiver adapted for immersion in said oil, first diluent and second diluent mixture, means for measuring electrical conductivity of fluid between said electrodes, and

neans for draining the mixture from said sample receiver.

11. The apparatus of claim 10 wherein the first menioned valve, pump, first diluent metering means, second liluent metering means, electrodes and draining means are each electrically connected to an automatic timer and programmer.

12. Automatic apparatus for use in intermittently analyzing liquid flowing through a pipeline at elevated pressures comprising a first conduit having an inlet end and outlet end adapted for connection to a pipeline at ongitudinally spaced locations and for continuously bypassing therethrough a portion of the stream of liquid lowing in such line, a reciprocating piston pump for netering a predetermined quantity of oil sample, a second conduit having a solenoid valve therein communicatng with said first conduit and the pump inlet, a sample eceiver having means for draining liquid contents therefrom, a third conduit having a pressure responsive valve herein communicating with the pump outlet and the sample receiver, said pressure responsive valve actuatable to permit liquid to flow from the pump to the sample receiver when the pressure in said third conduit between the pump outlet and pressure responsive valve s greater than the pressure in the pipeline, means for netering and transferring a predetermined quantity of a first liquid diluent into said sample receiver, means for netering and transferring a predetermined quantity of a second liquid diluent to said sample receiver, a stirrer n said sample receiver and means for actuating said stirrer, a pair of spaced electrodes adapted to contact the liquid in said sample receiver, means for measuring the electrical conductivity of liquid in said sample receiver, program timer means operatively connected to the pump, solenoid valve, sample receiver draining means, first diluent metering means, stirrer, second diluent metering means and the means for measuring electrical conductivity of the liquid, said program timer having means for actuating the pump, solenoid valve, first diluent transfer means and stirrer before transfer of the second diluent in said sampler receiver, said timer having means for actuating the electrical conductivity measuring means after the oil, first diluent and second diluent have been mixed with the stirrer to form a homogeneous mixture, and wherein said timer has means for actuating the sample receiver draining means at the end of each intermittent analysis.

13. The apparatus of claim 12 including means for injecting the liquid mixture into said first conduit downstream of said second conduit, said timer having means for actuating the injecting means after actuating the conductivity measuring means.

14. Apparatus according to claim 10, in which the means for draining the mixture from the sample receiver includes a positive displacement discharge pump, conduit means for conducting oil from the sample receiver to the discharge pump inlet, conduit means for conducting oil from the discharge pump outlet to the source of oil and a normally closed pressure responsive valve in the last mentioned conduit means actuatable at a pressure above that in said source.

References Cited by the Examiner

UNITED STATES PATENTS

2,607,718	8/52	Suthard	324—30 X
2,765,219	10/56	Shawhan	324—30 X
2,782,151	2/57	Suthard.	
2,950,177	8/60	Brown et al.	324—30
3,014,178	12/61	Dunn	324—30

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