

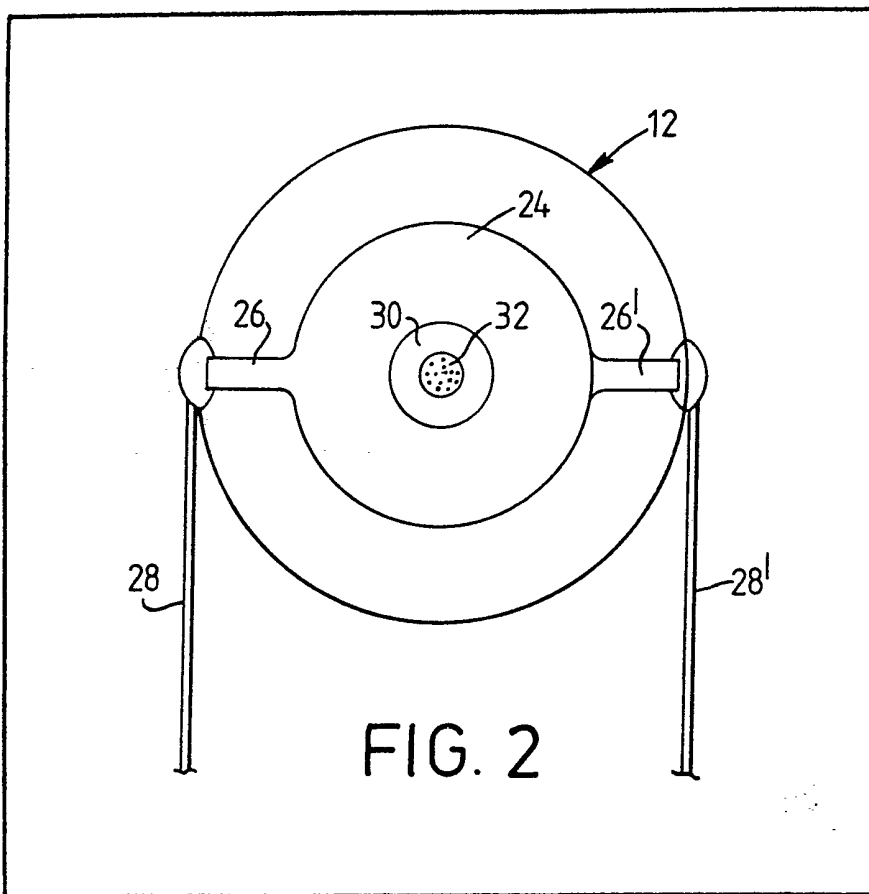
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(54) **Piezoelectric Gum-measurement Device**

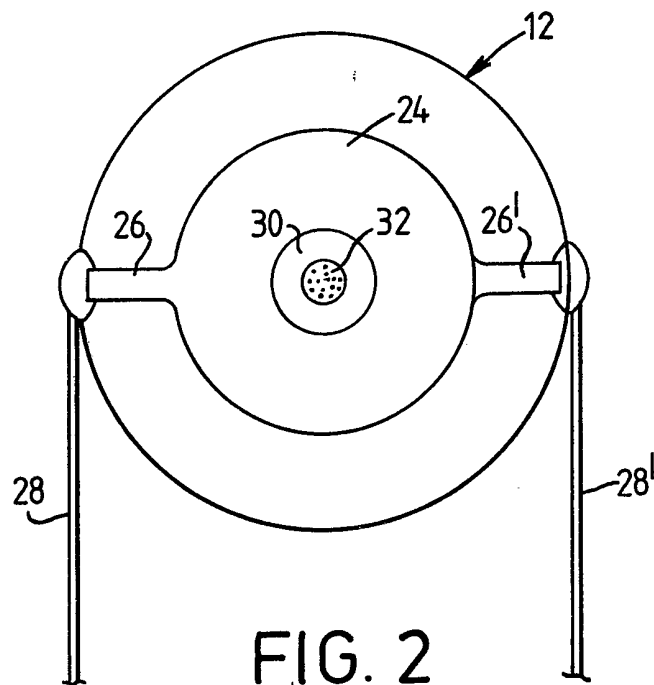
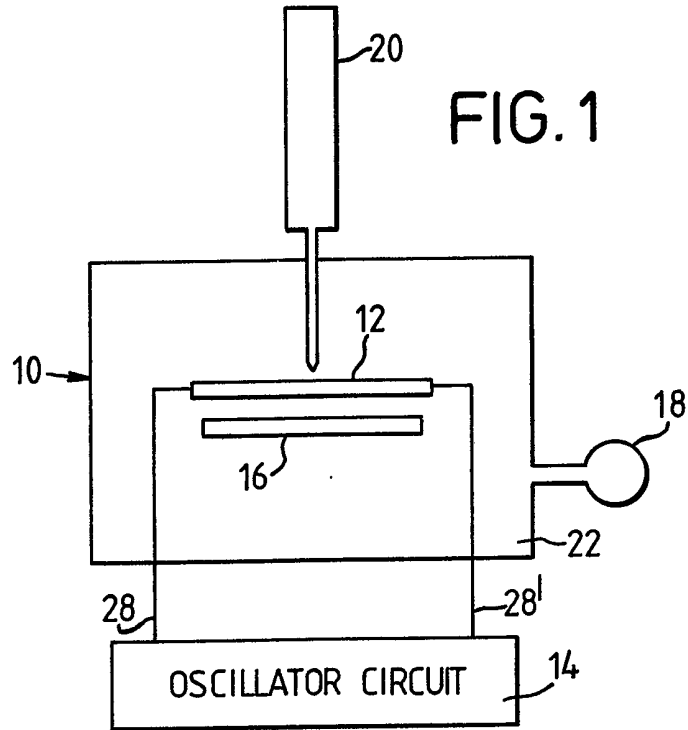
(57) Apparatus for measuring high-boiling components, especially existent gum levels in a petroleum hydrocarbons liquid, e.g. aviation fuel comprises: a piezoelectric crystal 12; a metallic electrode coating 24 on the crystal and a polytetrafluorethylene, or other lipophobic material, coating 30 centrally placed on electrode 24. The coating 30 is annular, defining a central sample-testing area 32 of uncoated electrode, or could be disc-

shaped. Electrode arms 26, 26' connect via leads 28, 28' with an oscillator circuit means. The crystal is placed test-surface uppermost in an evacuable housing containing a heater.

In use, a sample of liquid is placed on test area 32, heated and evaporated under vacuum, and the sonant frequency change between the crystal without sample and crystal with sample is observed. The result is then converted to existent gum level by reference to predetermined calibration data.



The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy



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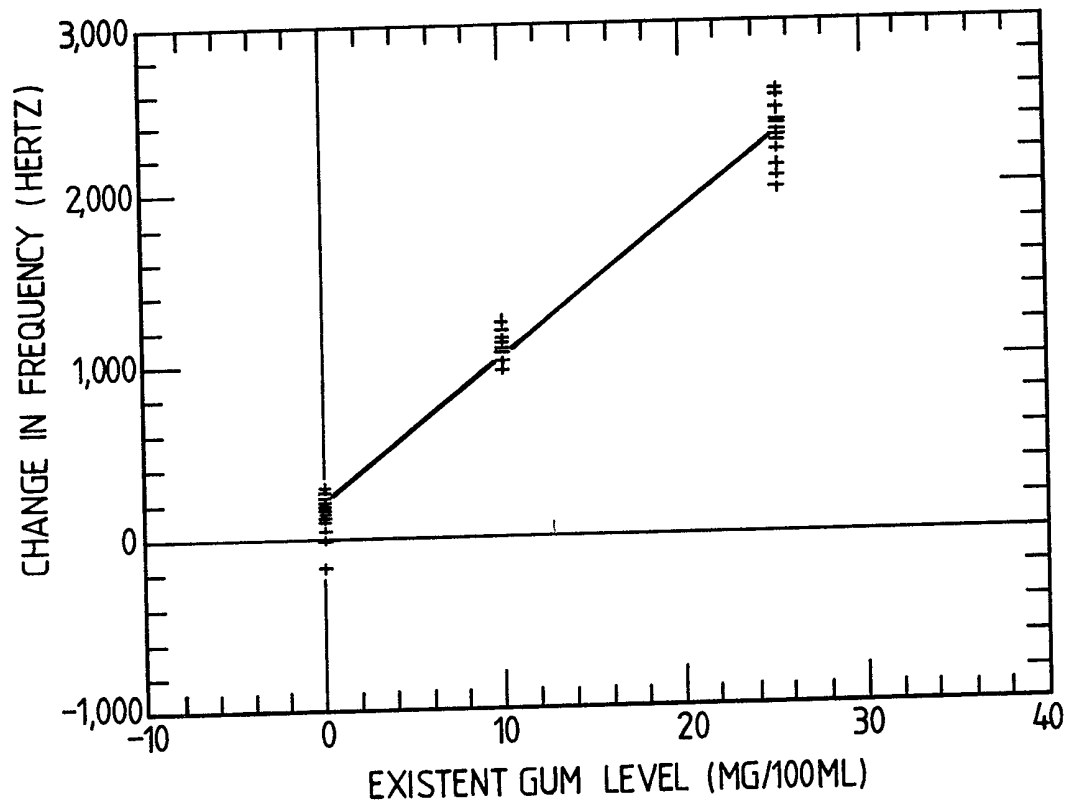


FIG. 3

SPECIFICATION

Piezoelectric Gum-Measurement Device

This invention relates to an apparatus and method for measuring the existent gum level of a liquid, more especially a petroleum hydrocarbons liquid, for example aviation fuels or gasolines. The term existent gum level is used herein to mean the residue from the evaporation of a sample of the liquid.

A variety of methods has been used in the analysis of petroleum hydrocarbons including gas chromatography, mass spectrometry, infrared spectrometry, ultraviolet spectrometry, X-ray analysis including X-ray fluorescence, X-ray diffraction and X-ray absorption, and electron microscopy. A number of different instruments have been developed using one or more of these or other methods.

Historically, existent gum levels in aviation fuels have been measured because there tends to be a relationship between the levels of existent gum and fuel purity. An increase in these gum levels from the refinery certification level usually means product contamination has occurred and the fuel may contain an unacceptable amount of "heavy ends".

The current technique for measuring existent gum in fuels is the jet method described in ASTM D381—70. In this method a measured quantity of fuel is evaporated under controlled conditions of temperature and flow of air or steam. The resulting evaporation residue from an aviation gasoline or an aircraft turbine fuel is weighed and the result reported as milligrams per 100 ml. For a motor gasoline, the evaporation residue is weighed before and after extracting with n-heptane and the result reported in milligrams per 100 ml. Although this method does provide an adequate and reliable determination of existent gum levels in fuels, it is somewhat cumbersome and inconvenient to run since it involves relatively large pieces of equipment requiring substantial capital investment as well as needing technically skilled personnel to carry out. Because of this, the test generally cannot be performed at individual field locations or terminals but at a central laboratory which involves the added cost of space and storage as well as a loss of time.

Accordingly, there is a need for a simplified, quicker and less complicated technique for measuring existent gum levels in fuels, which will require less burdensome apparatus with respect to size and investment. The availability of such a technique and apparatus will permit testing at various locations in the field rather than at a central laboratory and therefore ease the problem of determining off spec quality and allow for quicker correction.

The use of piezoelectric crystals for the selective analyses of fluid mixtures has been known in the art for some time. The basic principle involved in using a piezoelectric crystal as a detection device involves measuring the mass change of a vibrating crystal. There are two

65 modes in which the crystal is employed. Most involve the use of a predeposited substrate on the crystal to absorb the material to be analyzed. As the substrate or coating of the crystal interacts with another material and thus changes weight, 70 the change in weight or mass can be detected and used for determining qualitatively and quantitatively various components present. One patent which discloses coated piezoelectric analyzers is U.S. Patent 3,164,004 by William H. King. Another is U.S. Patent 3,427,864, wherein 75 the presence of moisture in a fluid mixture is detected using a piezoelectric crystal coated with a deliquescent salt such as lithium chloride. A variation of this technique is disclosed in U.S. Patent 3,260,104, and U.S. Patent 3,266,291, 80 which show an analyzer having two detection devices both having a piezoelectric crystal, one of which has a substrate selective to a particular material, and the other acting as a reference. The net output of the two detection devices is a measure of the interaction of at least one component to be detected. 85

Another method of using piezoelectric crystals as detection devices involves applications where the crystal is not coated with a substrate. This generally involves depositing a material mixed in solvent or other carrier on the crystal, evaporation of the carrier leaving behind the material of interest followed by measurement of crystal frequency. Methods of this type have been disclosed in U.S. Patents 3,856,466, and 3,863,495. 90

In the above-described techniques of using piezoelectric crystals, the sample location is dependent in the first case on the substrate coating amount and dimensions and the makeup of the surrounding materials; while in the second case it is dependent on the particular technique of sample application and control thereof. 100

Despite the longstanding use of piezoelectric crystals in detection devices, there is still a need for an apparatus and technique wherein sample location is readily controlled resulting in quick, accurate and consistent measurements of high-boiling components in liquids, especially existent gum levels in fuels. More especially, there is a need for a simplified, portable type apparatus useful in measuring gum levels in fuels in a quick manner at convenient locations. 105

The present invention provides an apparatus for measuring the existent gum level (as herein defined) of a liquid, for example a petroleum hydrocarbons liquid, which apparatus comprises:

(a) a pressure-tight housing adapted to be connected to means for reducing pressure in the housing; 120

(b) a piezoelectric crystal located within the housing with its upper surface in a substantially horizontal plane;

(c) piezoelectric detecting circuit components comprising electrode means on the crystal defining a metallic coating on at least part of the upper surface of the crystal, and electrical connection means extending in pressure-tight 125

manner from the electrode means to the exterior of the housing for connection to oscillator circuit means capable of measuring resonant frequencies of the crystal;

5 (d) a lipophobic coating on a part of the said metallic coating, which lipophobic coating defines a sample-testing area;

10 (e) pressure-tight opening/closing means on the housing for enabling a sample of the liquid to be tested to be introduced onto the sample-testing area; and

(f) heating means located within the housing for heating a liquid sample when present on the sample-testing area.

15 Preferably, the lipophobic coating is annular, whereby the sample-testing area is an area of the metal coating per se.

20 By forming such an annular area the sample will be repelled if it moves outside of the defined central area and thus will be confined to the desired area. The test area size may vary and to some extent will be limited by the technology available to custom coat the required area. Generally, a diameter up to about 0.40 inches (1 cm), preferably up to about 0.33 inches (8.0 mm), and more preferably up to about 0.3 inches (7.5 mm) inner diameter is utilized.

30 Another form of the lipophobic coating comprises a thin disc on the metal coating, which disc constitutes the sample-testing area. Again the preferred diameters will be as just described.

35 In all cases the lipophobic coating should be a thin film of sufficient thickness that the sample material will not spread but rather bead up in a mass and still allow the crystal to oscillate. The coating will generally be of a thickness of up to about 0.001 inches (0.025 mm).

40 Again, in all cases it is preferred that the sample-testing area should be at the centre of the crystal. It is indicated in U.S. Patent 3,856,466, using a non-coated crystal, that it is important to dispose samples in the centre of a crystal and in the same relative positions thereon. The present invention enables this to be easily achieved.

45 The lipophobic or repellent coating material that is used may be any substance which will adhere to the electrode coating and will repel the liquid sample. Additionally, it should resist removal by the washing fluid or solvent that is used to remove the samples. Generally, materials of this type are those that repel fats or similar substances. Such materials include, for example, Teflon (Registered Trade Mark), silicones, olefinic polymers, etc. with Teflon being particularly preferred.

55 The piezoelectric crystal used in this invention may be any responsive material which exhibits piezoelectric properties. The material exhibits piezoelectric properties if when subject to an electric potential it mechanically deforms and vice versa, when subject to a mechanical pressure it develops an electric potential. Several such materials are known; for example, crystals such as quartz, tourmaline Rochelle salts, barium titanate ceramic compositions, lead metaniobates and

lead zirconate-lead titanates. Quartz is the preferred crystal for use in the present invention.

70 The frequency at which a piezoelectric material, such as a quartz crystal, oscillates is dependent on several variables. These include the thickness of the crystal, the electrode structure, the characteristics of the oscillating circuit to which the crystal is connected, the temperature, and in the case of crystals, the particular axis
75 along which it is cut. The frequency, however, changes with corresponding change in the mass of the electrode. The slightest change in the electrode mass at an AT cut piezoelectric crystal will produce a detectable change in its resonant
80 frequency. Thus, it is generally accepted that a piezoelectric detecting circuit can detect a weight addition to the electrode surface of as little as 10^{-13} to 10^{-9} grams. Generally, piezoelectric crystals having a resonance frequency in the
85 range of 9MHz are suitable for use in this invention.

90 Preferably the metal(s) of the electrode coating on the piezoelectric crystal is/are of high electrical conductivity. In a preferred embodiment the coating comprises gold in contact directly with the quartz or other crystal and a nickel coating over the gold to make the exposed surface resistant to abrasion such as one might encounter in use.

95 The electrical connection means are adapted for connection to oscillator circuit means capable of measuring resonant frequencies of the piezoelectric crystal. The oscillator circuit means may if desired be connected so that the apparatus
100 of the invention then additionally comprises that circuit means. In use, the oscillator circuit means will obtain the resonant frequency from the crystal containing sample material. The oscillator circuit produces a radio frequency signal, usually about 9 to 27 megahertz, which can be converted to an audio frequency signal and which in turn can be transmitted to a standard frequency converter. The converter changes the audio frequency signal into an analog or digital signal and such analog or digital signal is transmitted to an output circuit in either analog or digital form and more commonly the output comprises an analog signal which manifests itself as a needle indicator or a conventional microammeter meter.
115 By converting the audio frequency signal, the converter thereby emits a signal which is available for reading with a frequency counter at the output.

120 It should be appreciated that the oscillator circuits employed in the instant invention are well known in the art and obviously, various suitable standard oscillator circuits may be employed. It should be emphasized that the particular type of oscillator circuit with which the crystal is
125 connected is not critical. Well-known oscillators which may be used include the Hartley oscillator and its many modifications, the tuned grid-tuned plate oscillator, the Dynatron oscillator, the transition oscillator and many other forms of
130 feedback oscillators. Similarly the converters and

counters used in the circuit are well known in the art and thus any of such known units may be employed in the present invention.

Preferably the heating means for evaporating the liquid is a heater of the resistance type, placed in close proximity to the crystal. Generally the voltage of the heater will be placed at a level to provide adequate heat to evaporate the fuel but not so much as to make the crystal unstable or fail to resonate.

The housing of the apparatus is adapted for connection to pressure-reducing means, such as an evacuator or vacuum pump. This not only helps speed up the evaporation of the sample but it has been found that such means allows the operation to be conducted at a lower temperature, shortens the time needed to conduct the test and gives better, more accurate results. A variety of vacuum pumps, many of which are conventional and commercially available, may be used in this invention. The housing is preferably thermally insulated to assist in maintaining substantially standard, repeatable operating conditions in different ambient conditions.

The invention will now be further described, in a non-limitative manner, with reference to the accompanying drawings, in which:

Figure 1 illustrates schematically the overall arrangement of an embodiment of apparatus according to the present invention;

Figure 2 illustrates, in generally plan view, one embodiment of a piezoelectric crystal, with electrode and lipophobic coatings, used in the present invention; and

Figure 3 is a graphical illustration of frequency change versus existent gum level in mg gum/100 ml jet fuel.

In the embodiment shown in Figure 1 a light weight pressure-tight housing 10 of machine metal contains supported substantially horizontally therein a quartz piezoelectric crystal 12. Leads 28, 28' from the crystal 12 (which latter is explained hereafter with reference to Figure 2) exit in pressure-tight manner from housing 10. In the embodiment illustrated in Figure 1 the leads are shown connected to oscillator circuit means 14, which may be of any of the types hereinbefore recited.

The embodiment in Figure 1 is shown coupled to pressure-reducing means 18, suitably an evacuator or vacuum pump.

A resistance heater 16 is supported in proximity to the underside of crystal 12 to provide for evaporating a liquid test sample. The test sample can be introduced through a pressure-tight opening/closure in the housing 10 by means of a sample holder or supply device 20. Any sample supply means may be used although, preferably, a syringe or needle-type apparatus with a tube for holding sample can be used. The sample supply means 20 is thus placed in the same position relative to the crystal each time a new sample is being added. A suitable holding means, not shown, may be attached to the

housing 10 to hold the sample supply means 20 in place.

Referring now to Figure 2, the piezoelectric crystal 12 is disc-shaped and carries on its upper surface a disc shaped metal coating electrode 24. The electrode has a crystal contacting surface of gold and a covering thereover of nickel. On its central portion the electrode 24 carries an annulus 30 of polytetrafluorethylene (such as that sold in conjunction with the name Teflon, the word "Teflon" being a registered Trade Mark). The annulus is up to 0.025 mm thick and about 8 mm in internal diameter. The central area of the annulus, that is to say a disc 32 of un-coated electrode, constitutes a sample-testing area.

Electrode 24 is connected via narrow conducting strips 26, 26' and the leads 28, 28' to the oscillator circuit means 14 (Figure 1).

Other components may also be employed in conjunction with the apparatus of this invention, including, for example, timer means and an aspirator and charcoal canister.

A method of measuring the existent gum level of, for example, a fuel comprises first cleaning a crystal with a solvent, for example as chloroform or acetone, and then placing the cleaned crystal into place in the described apparatus and allowing to dry.

The crystal must first be calibrated using a number of fuels having known existent gum levels, such as fuels with added contaminants. It is necessary, of course, to select fuels as standards which will cover the range of frequency expected for the fuels to be tested. A measured amount of standard fuel sample, i.e. 10 ml, is applied to the crystal using the syringe device illustrated in Figure 1.

A plot (Figure 3) of resulting frequency change vs. existent gum level is made for the fuels with known existent gum levels, e.g. jet fuel doped with 0, 200 and 500 ppm Bright Stock (about 0, 10 and 25 mg existent gum/100 ml fuel respectively), using an average of two determinations for each point with the resulting calibration line being fitted to the data using the method of least squares. Frequency change is the difference between the frequency of the clean crystal (without sample) and the frequency of the crystal with sample thereon. A sample of test fuel is then placed in a like manner in the apparatus, and the resulting change in frequency determined. Using the predetermined calibration plot (Figure 3), the amount of existent gum can then be established. For example, a test sample showing a frequency change of about 1200 hertz would have an existent gum level of about 11.9 mg/100 ml using predetermined calibration plot, Figure 3.

The apparatus of this invention provides for a simplified and quick technique for measuring high-boiling components in fuels and particularly allows for results which are quite accurate. In prior art analyzers which use crystals coated with a substrate for absorbing material, the amount of substrate is a significant variable and its volume, thickness, weight and location on the responsible

crystal material are of significance in determining the response of the detector.

The use of the apparatus of this invention overcomes many of the problems associated with the earlier type analyzers and furthermore provides a relatively simple, yet accurate and quick technique for measuring high-boiling components in fuels. One significant advantage of this apparatus is its ready accessibility which allows for measurement at convenient locations in the field.

Claims

1. An apparatus for measuring the existent gum level (as herein defined) of a liquid, for example a petroleum hydrocarbons liquid, which apparatus comprises:

(a) a pressure-tight housing adapted to be connected to means for reducing pressure in the housing;

(b) a piezoelectric crystal located within the housing with its upper surface in a substantially horizontal plane;

(c) piezoelectric detecting circuit components comprising electrode means on the crystal defining a metallic coating on at least part of the upper surface of the crystal, and electrical connection means extending in pressure-tight manner from the electrode means to the exterior of the housing for connection to oscillator circuit means capable of measuring resonant frequencies of the crystal;

(d) a lipophobic coating on a part of the said metallic coating, which lipophobic coating defines a sample-testing area;

(e) pressure-tight opening/closing means on the housing for enabling a sample of the liquid to be tested to be introduced onto the sample-testing area; and

(f) heating means located within the housing for heating a liquid sample when present on the sample-testing area.

2. An apparatus as claimed in claim 1, wherein the lipophobic coating is annular, whereby the sample-testing area is an area of the metal coating per se.

3. An apparatus as claimed in claim 1, wherein the lipophobic coating comprises a thin disc on the metal coating, which disc constitutes the sample-testing area.

4. An apparatus as claimed in claim 2 or claim 3, wherein the lipophobic coating has a thickness of not more than 0.025 mm.

5. An apparatus as claimed in any one of claims 2 to 4, wherein the sample-testing area has a diameter up to 1 cm.

6. An apparatus as claimed in any one preceding claim, wherein the sample-testing area is located substantially at the centre of the piezoelectric crystal.

7. An apparatus as claimed in any preceding claim, wherein the lipophobic coating is polytetrafluorethylene, a silicone or an olefin polymer.

8. An apparatus as claimed in any preceding

claim, wherein the piezoelectric crystal is a quartz crystal.

9. An apparatus as claimed in any preceding claim, wherein the metallic coating comprises a layer of gold in contact with the crystal and a covering of nickel over the gold.

10. An apparatus as claimed in any preceding claim and connected to oscillator circuit means capable of measuring resonant frequencies of the piezoelectric crystal.

11. An apparatus as claimed in any preceding claim and connected to means for reducing the pressure within the housing.

12. An apparatus as claimed in claim 1 and substantially as herein described.

13. An apparatus as claimed in claim 1 and substantially as herein described with reference to Figure 1 or Figure 2 of the accompanying drawings.

14. A method of measuring the existent gum level (as herein described) in a liquid, for example a petroleum hydrocarbons liquid, substantially as herein described with reference to the accompanying drawings.

New Claims or Amendments to Claims filed on 2 October 1980.

Superseded Claims 1

New or Amended Claims:—

1. An apparatus for measuring the existent gum level (as herein defined) of a liquid, for example a petroleum hydrocarbons liquid, which apparatus comprises:

(a) a pressure-tight housing adapted to be connected to means for reducing pressure in the housing;

(b) a piezoelectric crystal located within the housing with its upper surface in a substantially horizontal plane;

(c) piezoelectric detecting circuit components comprising electrode means on the crystal defining a metallic coating on at least part of the upper surface of the crystal, and electrical connection means extending in pressure-tight manner from the electrode means to the exterior of the housing for connection to oscillator circuit means capable of measuring resonant frequencies of the crystal;

(d) a lipophobic coating on a part of the said metallic coating, which lipophobic coating defines a sample-testing area;

(e) pressure-tight opening/closing means on the housing for enabling a sample of the liquid to be tested to be introduced onto the sample-testing area;

(f) heating means located within the housing for heating a liquid sample when present on the sample-testing area; and

(g) means for reducing the pressure within the housing.

11. An apparatus as claimed in claim 1 and substantially as herein described.

12. An apparatus as claimed in claim 1 and substantially as herein described with reference to

Figure 1 or Figure 2 of the accompanying drawings.

13. A method of measuring the existent gum level (as herein described) in a liquid, for example

5 a petroleum hydrocarbons liquid, substantially as herein described with reference to the accompanying drawings.

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