United States Patent [19]

Gregory et al.

[11] **3,842,270**

[45] **Oct. 15, 1974**

[54] **PRESSURIZED OIL-IN-WATER MONITOR**

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[22] Filed: **Oct. 29, 1973**

[21] Appl. No.: **410,850**

[52] **U.S. Cl.** **250/301,** 250/365, 250/461

[51] **Int. Cl.** **G01n 21/34**

[58] **Field of Search** 250/301, 304, 365, 461

[56] **References Cited**

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2,591,737 4/1952 Souther, Jr. .... 250/301 X

2,852,693 9/1958 Hughes et al. 250/301

FOREIGN PATENTS OR APPLICATIONS

1,161,916 8/1969 Great Britain 250/301

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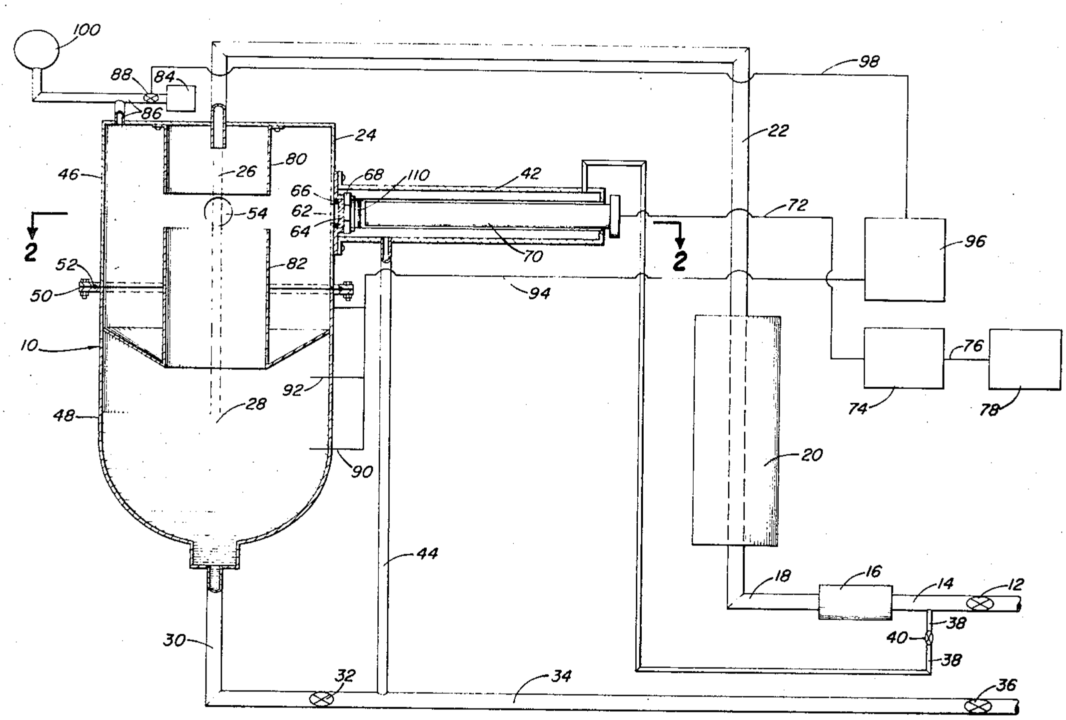
[57] **ABSTRACT**

Method and apparatus for monitoring the presence in an aqueous medium of an oil which fluoresces when irradiated by ultraviolet light wherein the fluid stream being monitored does not come in direct contact with the light source or detection means.

13 Claims, 4 Drawing Figures



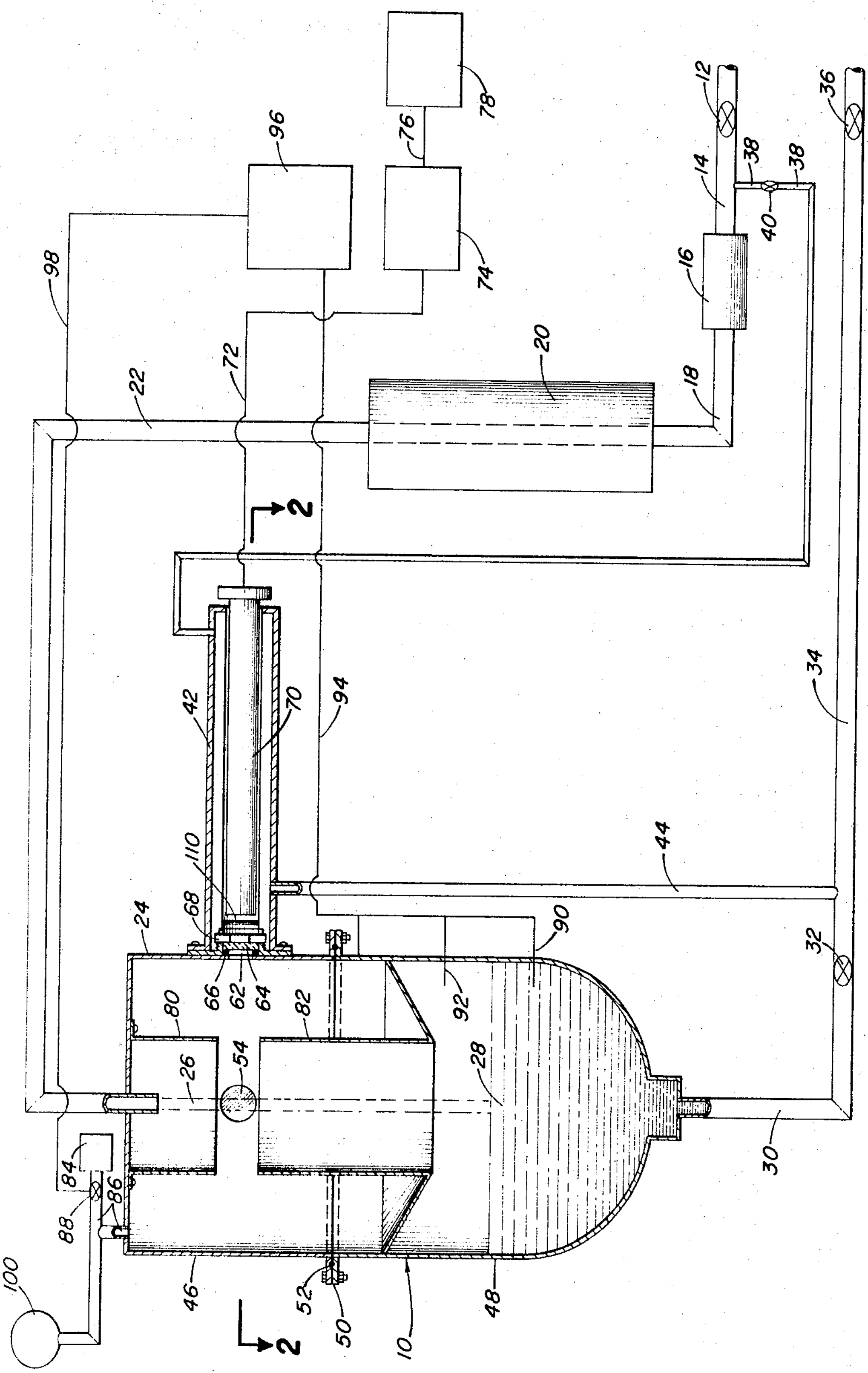

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FIG. 1

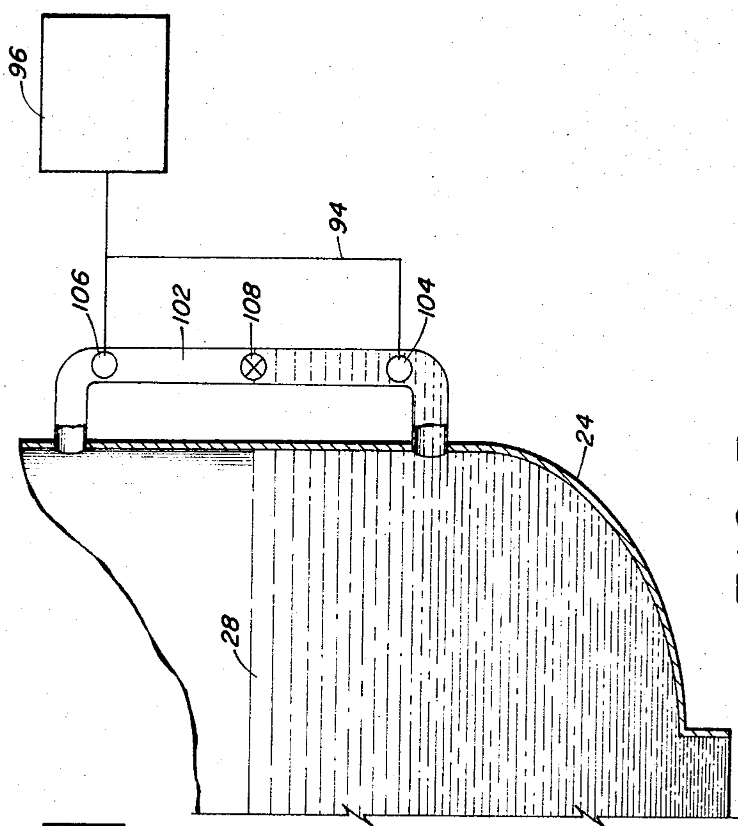

FIG. 3

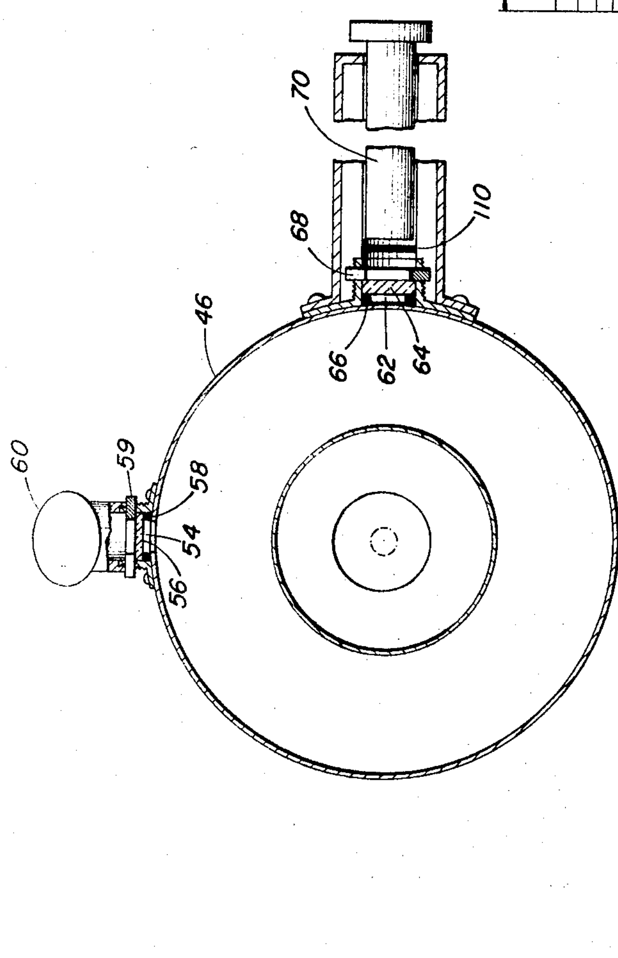

FIG. 2

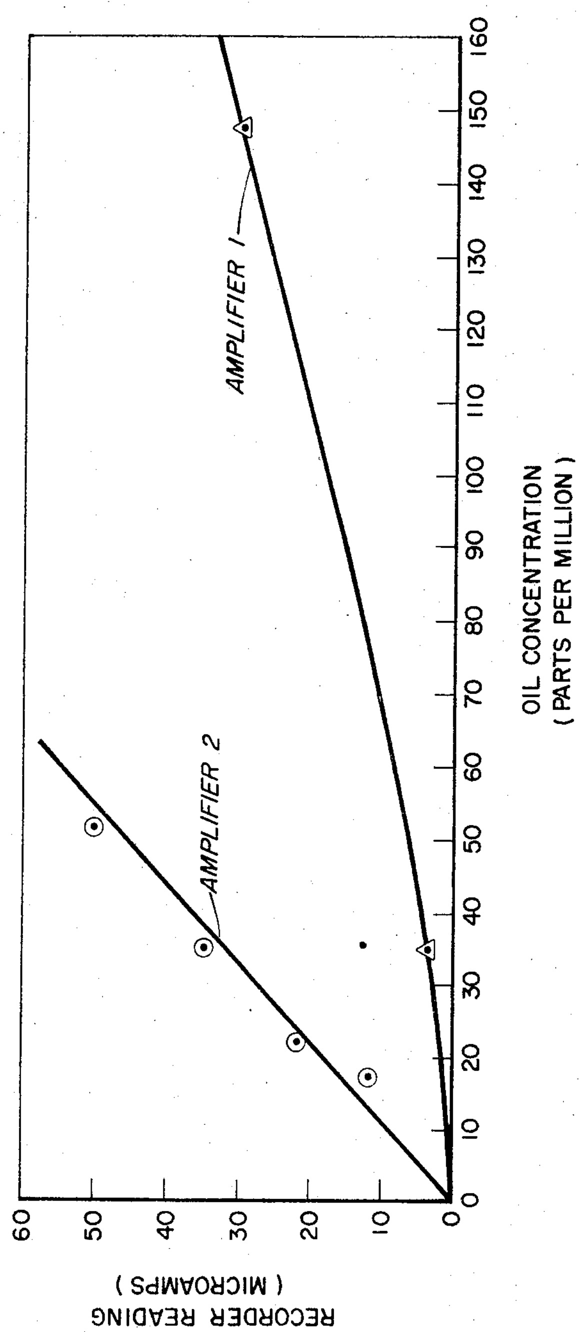
AMPLIFIER 1
AMPLIFIER 2
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
OIL CONCENTRATION
(PARTS PER MILLION)
0 10 20 30 40 50 60
RECORDER READING
(MICROAMPS)

FIG. 4

PRESSURIZED OIL-IN-WATER MONITOR

BACKGROUND OF THE INVENTION

a. Field of the Invention

The present invention relates to a method and apparatus for moniotring the presence in an aqueous medium of a material which fluoresces when exposed to ultraviolet light. More particularly, it relates to such a method and apparatus which operate under pressurized conditions.

b. Description of the Prior Art

Various aqueous base liquid streams which are handled in industrial processes also contain minor proportions of oleaginous base materials. It is oftentimes desirable to determine the presence of and concentration of such oleaginous base materials. Many oleaginous base materials fluoresce when exposed to ultraviolet light, emitting visible light. Thus, detection methods and apparatus have developed wherein a beam of ultraviolet light is cast on a liquid stream and the amount of visible light emitted, if any, detected. In one type of apparatus, the liquid stream is passed through a glass cell with the ultraviolet light beam and the emitted visible light passing through the glass. However, in such an apparatus, the liquid continually contacts the glass and the oleaginous materials tend to gradually coat the glass surface causing the apparatus to give a falsely high reading for the oleaginous materials. There also has been used a similar apparatus employing light detection in which the stream of liquid being monitored does not touch the ultraviolet light source or visible light detection means. Such an apparatus is described in U.S. Pat. No. 3,581,085 issued May 25, 1971, to Barrett. In this apparatus, the liquid stream to be monitored falls down a tube without touching the sides of the tube, collects in the bottom of the tube and is discharged. The space between the falling liquid stream and the sides of the tube is occupied by air. The ultraviolet light source and visible light detection means are mounted outside the tube opposite holes in the tube. This apparatus functions during its initial phase of operation without any coating of the light source or detection means by the liquid being monitored. However, it has been found that the falling stream of liquid tends to entrain and dissolve some of the air occupying the space between the stream of liquid and the sides of the tube, carries this air to the bottom of the tube and on out of the tube. Thus, as operation of the apparatus proceeds, the amount of air in the tube steadily decreases. The height of the pool of liquid collecting in the bottom of the tube rises to fill the space formerly occupied by the air until liquid reaches the level of the light source and detecting means, contaminates the same with oleaginous material and renders further monitoring possible.

It is an object of this invention to provide a method and apparatus for monitoring the presence of an oleaginous fluorescing material in an aqueous liquid.

It is a further object to provide such a method and apparatus which provide continuous monitoring on a stream of such liquid.

It is a still further object to provide an apparatus for such monitoring utilizing a light source and detection means wherein the liquid to be monitored initially does not directly contact the light source detection means.

It is another object to provide means for keeping the liquid out of direct contact with the light source and detection means throughout the operation of the apparatus.

Other objects, advantages, and features of the invention will become apparent from the following specification and appended claims.

BRIEF SUMMARY OF THE INVENTION

This invention involves a method and apparatus for continually monitoring an oleaginous material which fluoresces when exposed to ultraviolet light, which oleaginous material is present in an aqueous base liquid comprising:

a. a tubular housing through which falls a stream of liquid to be monitored, such housing having an internal diameter greater than the diameter of the falling stream of liquid to provide an air annulus therebetween, a bottom section of reduced diameter in which the stream of liquid collects before passing out of the housing and two sealed windows at the same horizontal level in the upper portion of the lateral sidewall of the housing,

b. means for introducing a stream of liquid into the upper portion of the housing so that such liquid falls through the housing without touching the lateral sidewalls thereof,

c. means for introducing a beam of ultraviolet light through one of the windows in the housing and into the falling stream of liquid,

d. means for detecting fluorescence radiation mounted outside the housing opposite the other window in the housing,

e. means for detecting the height of the column of liquid which collects in the bottom portion of the housing, and

f. means for injecting a gas into the air annulus in the housing before the height of the column of liquid which collects in the bottom portion of the housing reaches the level of the windows in the lateral sidewalls of the housing.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a cross sectional schematic view of the apparatus of this invention.

FIG. **2** is a cross sectional schematic view of the main body of the subject apparatus of FIG. **1** taken along the Plane **2—2** of FIG. **1.**

FIG. **3** is a cross sectional schematic view of an alternate embodiment of the fluid level control means.

FIG. **4** is a graph illustrating the calibration of the apparatus of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to FIGS. **1** and **2,** the apparatus, generally denoted by Reference **10,** comprises means for supplying a stream of fluid to be monitored such as Valve **12** through which the composition to be monitored enters and preferably passes through inlet tube **14.** The main body of the composition passes through flow controller **16** and tubing **18** into rotameter **20** which measures the rate of flow.

From rotameter **20,** the main body of composition passes through tubing **22** into the top of housing **24.** The composition then falls through housing **24** as stream **26** collects in the bottom of housing **24** and forms fluid column **28.** The composition drains from the bottom of housing **24** and is withdrawn from the apparatus via tubing **30**, valve **32**, tubing **34**, and valve **36**. It is preferred that a small portion of the composition be withdrawn from tubing **14** via tubing **38** and valve **40**, passed through constant temperature jacket **42** and then through tubing **44** which discharges into tubing **34**.

Housing **24** is conveniently made in upper section **46** and lower section **48** connected by flange **50** and sealing mecnanism **52** such as an O-ring. Housing **24** is provided with first aperture **54**, covered by transparent window **56** which may be made of quartz, glass or other solid transparent to light. Sealing mechanism **58**, such as an O-ring, is provided between housing **24** and transparent window **56**. Transparent window **56** is held in position by locking mechanism **59**, such as a locking nut. A source of ultraviolet radiation **60** is positioned outside housing **24** and located so as to pass a beam of ultraviolet radiation through the transparent window **56** and through composition stream **26**.

Housing **24** is also provided with second aperture **62** positioned at the same height as first aperture **54** and at any position around the circumference of housing **24**, preferably at right angles to first aperture **54**.

This universal positioning of aperture **62** with respect to aperture **54** is made possible by a filter **110** in the photocell detector **70** that keeps the incident ultraviolet light from activating the photocell. The only light that may enter the photocell detector **70** is long wavelength fluorescent light the intensity of which is proportional to the contaminant concentration in the stream to be monitored. Thus, photocell detector **70** detects the fluorescence radiation created by ultraviolet light striking composition stream **26**. This is generally visible light.

Second aperture **62** is covered by transparent window **64**. Sealing mechanism **66**, such as an O-ring, is provided between housing **24** and transparent window **64**. Transparent window **64** is held in position by locking mechanism **68**, such a locking nut. Visible light detecting means **70**, such as a photocell, is positioned outside housing **24** behind transparent window **64**. Visible violet light detecting means **70** is surrounded by constant temperature jacket **42** which decreases fogging of transparent window **64** which can occur during operation of the apparatus in the absence of constant temperature jacket **42**. The fluorescent light transmitted from stream **26** is picked up by visible light detecting means **70** and the results observed visually or recorded on a suitable recording means, such as wires **72** which connect visible light detecting means **70** to amplifier **74** which in turn is electrically connected by wires **76** to recorder **78**.

It is preferred that housing **24** be provided with splash guard means **80** and **82** positioned between the lateral sidewall of housing **24** and stream **26**. Upper splash guard means **80** is preferably a hollow cylinder attached to the top of housing **24** and provides a shroud around the upper portion of stream **26**. The bottom of upper splash guard **80** is just above apertures **54** and **62**. Lower splash guard **82** is preferably a hollow cylinder attached to the lateral sidewall of housing **24** at a point below apertures **54** and **62**. The top of lower splash guard **82** extends to just below apertures **54** and **62**. The function of splash guards **80** and **82** is to reduce the amount of liquid from stream **26** and fluid column **28** that splashes onto transparent windows **56** and **64** during operation of the apparatus.

It was experienced during operation of the apparatus as described above that falling stream **26** dissolved and entrained a portion of the air in the housing and carried this air with it into fluid column **28** and then on out of housing **24**. Thus, as the quantity of air in housing **24** decreased, the height of fluid column **28** would gradually rise in housing **24** until it reached the level of transparent windows **56** and **64** and cover the same, thus disrupting the desired observations. To prevent housing **24** from filling with liquid in this manner, it is necessary to inject gas into housing **24**. This can be done by constantly bleeding gas from gas supply **84** which is at a pressure above the pressure in housing **24** into housing **24** via tubing **86** and control valve **88**. Preferably gas is intermittently injected into housing **24** before the height of fluid column **28** gets dangerously close to transparent windows **56** and **64**. The intermittent injection can be achieved by a means for detecting the height of fluid column **28** in housing **24** which controls means for injecting gas into housing **24**. The means for detecting the height of fluid column **28** in housing **24** can be lower level conductance probe **90** and upper level conductance probe **92**. These level probes extend through the side of housing **24**. Lower level probe **90** is positioned near the bottom of housing **24**. Upper level probe **92** is vertically positioned therefrom at a point below transparent windows **56** and **64**. Lower level probe **90** and upper level probe **92** are electrically connected by wire **94** to level controller **96**. Level controller **96** is electrically connected by wire **98** to solenoid valve **88** which controls flow of gas from gas supply **84** into housing **24**. Pressure gauge **100** indicates the pressure in the housing. The pressure inside housing **24** should be maintained about 10 psi above the pressure downstream of monitor **10**. When the height of fluid column **28** rises in housing **24** and touches upper level probe **92**, level controller **96** opens solenoid valve **88** allowing gas to flow into housing **24**, thus depressing the height of fluid column **28**. When the height of fluid column **28** falls in housing **24** below lower level probe **90**, level controller **96** closes solenoid valve stopping flow of gas into housing **24**.

An alternate means for detecing the height of fluid column **28** in housing **24** comprises a sight gauge means such as shown in FIG. **3** wherein hollow sight gauge column **102** connected to the interior of housing **24** at its upper and lower end is provided with lower light source and photocell combination **104**, upper light source and photocell combination **106** and opaque ball **108** which floats on fluid column **28** extending into the sight gauge means. Lower light source and photocell combination **104** and upper light source and photocell combination **106** are electrically connected by wire **94** to flow controller **96**. When the height of fluid column **28** rises so that opaque ball **108** interrupts light between upper light source and photocell combination **106**, level controller **96** opens solenoid valve **88** allowing gas to flow into housing **24**. When the height of fluid in column **28** falls so that opaque ball **108** interrupts light between lower light source and photocell combination **104**, level controller **96** closes solenoid valve **88** stopping flow of gas into housing **24**.

The apparatus of this invention can be used to monitor the presence in an aqueous medium of small concentrations of an oleaginous material which fluoresces when irradiated by ultraviolet light (220 to 350 nanometers. The oleaginous material may be a petroleum oil such as crude oil or any fraction or refined product thereof. The compounds most responsible for fluorescence in oil are the polynuclear aromatics. The fluorescent yield of an oil depends both upon the polynuclear aromatic content and upon the kinds of molecules comprising the polynuclear aromatics. The size of oil particles injected into the optical path has an effect on fluorescent intensity. Above 5 microns variation in particle diameter will result in fluctuations of the output signal due to surface effects. Below 5 microns in diameter, particles become essentially transparent and fluorescence becomes independent of particle size. If the fluid to be monitored contains oil particles having a diameter of more than 5 microns, it is preferred to pass the fluid through a high shear pump positioned upstream of the monitor to create smaller dispersed oil droplets with a narrower drop size distribution.

The gas injected into the housing to supress the column of liquid in the housing can be any gas which is inert to the falling stream of liquid. Suitable gases include air, oxygen, carbon dioxide, combustion gases, nitrogen, argon, and similar inert gases. The aqueous base fluid may be water or any brine.

EXAMPLE

An apparatus was assembled as described above using ½-inch diameter tubing **22** to introduce the fluid stream into housing **24** at the rate of 1 gallon per minute. The pressure in housing **24** was regulated by ball valve **32** to a pressure 10 pounds per square inch above the system into which the fluid is being discharged through valve **36.** Conductance probes **90** and **92** were insulated from the metal of housing **24** by drilled-out fittings of nylon, a non-conductor. Conductor probes **90** and **92** were coated by a thin coating of epoxy resin, a non-conductor, except for one-half inch on each end. Probes **90** and **92** were O-ring sealed in the nylon fittings. As the signal from the photocell is sometimes weak if the concentration in the aqueous medium of materials which fluoresce is small, it is preferred to use an amplifier. In these tests, three-decade amplifier **74** which contained a potentiometer for setting the zero point recorder **78** was used. 1,000-ohm single channel micro-ampere recorder **78** was used with a recorder chart speed of one inch per hour to give a one-month life expectancy to each roll of chart paper. The mercury lamp ultraviolet light source exhibits its greatest intensity at 254 nm with less intense spectral lines occurring up to 577 nm. To initiate fluorescence in a molecule, the exciting wavelength must be within a certain energy range characteristic of the molecule. Most dark crude oils fluoresce most intensely when excited with energy in the 300 to 400 nm range. Thus, the spectrum of the mercury lamp was altered by using two filters. One filter was used to shift the 254 nm peak to 366 nm. A band pass filter was used to limit the emiitted light to the 300 to 400 nm range.

The monitor was calibrated by passing a series of streams of fluid of varying oil concentration through the monitor and plotting the results of the recorder reading for each versus oil concentration as determined by some standard analytical technique. The monitor was installed on a water line entering a waterflood injection tank. The water was water which had been produced from an oil producing well, separated as nearly as possible from the oil and was being injected into a subterranean formation via another well to serve as a drive fluid in an effort to recover additional oil from the formation. The "water" contained some oil which had not been completely separated therefrom. Readings were obtained with amplifier set on 1 and 2. When fluctuations in the readings were observed, samples of the water passing through the monitor were obtained and the oil concentration thereof determined using a standard colorimetric method of analysis. FIG. **4** shows a plot of recorder readings versus oil concentrations obtained in the colorimetric analysis. For an amplifier setting of 2, the slope of the calibration curve was very nearly unity showing that each part per million of oil caused recorder response of 1 microamp. When the type of oil in the fluid being monitored changes, the monitor must be recalibrated.

Even though the foregoing discussion has described certain specific embodiments of this invention, it is to be understood that numerous other arrangements will be obvious to those skilled in the art which embody the principles of the invention and fall within the scope thereof.

We claim:

1. An apparatus for monitoring in an aqueous base fluid an oleaginous material which fluoresces when irradiated by ultraviolet light comprising:

a. a vertically positioned tubular housing means for receiving a stream of fluid to be monitored, said tubular housing means having an upper portion having an internal diameter greater than the diameter of the stream of fluid to provide an air annulus therebetween, a bottom section of reduced diameter in which the stream of fluid collects before passing out of the housing and a first and second sealed transparent windows at the same horizontal level in the upper portion of the lateral sidewall of the housing,

b. means for introducing a stream of fluid into the upper portion of said tubular housing means so that such fluid falls through said upper portion without touching the lateral sidewall thereof,

c. means for introducing a beam of ultraviolet light through one of the said sealed windows and into the falling stream of fluid,

d. means for detecting fluorescence radiation mounted outside said tubular housing means opposite the other of the said sealed windows,

e. a supply of gas at a pressure above the pressure in the tubular housing connected to the upper portion of the tubular housing.

2. An apparatus for monitoring in an aqueous base fluid an oleaginous material which fluoresces when irradiated by ultraviolet light comprising:

a. a vertically positioned tubular housing means for receiving a stream of fluid to be monitored, said tubular housing means having an upper portion having an internal diameter greater than the diameter of the stream of fluidid to provide an air annulus therebetween, a bottom section of reduced diameter in which the stream of fluid collects before passing out of the housing and a first and second sealed transparent windows at the same horizontal level in the upper portion of the lateral sidewall of the housing,

b. means for introducing a stream of fluid into the upper portion of said tubular housing means so that such fluid falls through said upper portion without touching the lateral sidewall thereof,

c. means for introducing a beam of ultraviolet light through one of the said sealed windows and into the falling stream of fluid,

d. means for detecting fluorescence radiation mounted outside said tubular housing means opposite the other of the said sealed windows,

e. means for detecting the height of the column of fluid which collects in the bottom section of said tubular housing, and

f. means for injecting a gas into the air annulus in said tubular housing when said height detecting means indicates that the height of said column of fluid is approaching the level of said windows.

3. The apparatus of claim **2** wherein the means for detecting the height of the column of fluid which collects in the bottom section of said tubular housing comprises two conductance probes mounted through the lateral sidewall of said tubular housing vertically spaced apart between the bottom section of said tubular housing and the said windows.

4. The apparatus of claim **2** wherein the means for detecting the height of the column of fluid which collects in the bottom section of said tubular housing comprises a sight gauge mounted in the lateral sidewall of said tubular housing between the bottom section of said tubular housing and the said windows.

5. The apparatus of claim **2** wherein the means for detecting the height of the column of fluid which collects in the bottom section of said tubular goods controls a solenoid valve which admits gas into the air annulus in said tubular housing.

6. The apparatus of claim **2** wherein the means for introducing a stream of fluid into the upper portion of said tubular housing means includes a flow controller to regulate the rate at which the stream of fluid falls through the tubular housing.

7. The apparatus of claim **2** wherein the first and second sealed windows are mounted at a right angle to each other in the tubular housing.

8. The apparatus of claim **2** wherein the means for detecting fluorescence radiation of (d) comprises a photocell positioned behind a filter which filters out incident ultraviolet light.

9. The apparatus of claim **2** wherein the tubular housing is provided with splash guards positioned between the lateral sidewall of the tubular housing and the falling stream of fluid which splash guards decrease splashing of the fluid onto the sealed transparent windows.

10. The apparatus of claim **2** wherein the fluorescence radiation detecting means of (d) is supplied with a constant temperature jacket maintained at the same temperature as the fluid stream.

11. A method for monitoring in an aqueous base fluid an oleaginous material which fluoresces when irradiated by ultraviolet light comprising:

a. injecting a fluid to be monitored into the upper portion of a vertically positioned tubular housing so that a stream of said fluid falls through the tubular housing without touching the lateral sidewall of said upper portion of the tubular housing,

b. collecting said fluid in the bottom portion of said tubular housing which bottom portion has a diameter which is smaller than the diameter of the upper section thereof,

c. discharging said fluid from said tubular housing,

d. irradiating said falling stream of fluid with ultraviolet light transmitted through a first transparent sealed window in the upper portion of said tubular housing,

e. detecting fluorescence radiation from said irradiated falling stream of fluid through a second transparent sealed window in the upper portion of the housing, and

f. injecting a gas into the upper portion of said tubular housing to suppress the height of the column of fluid collected in the bottom portion of the tubular housing below the level of the transparent sealed windows.

12. A method for monitoring in an aqueous base fluid an oleaginous material which fluoresces when irradiated by ultraviolet light comprising:

a. injecting a fluid to be monitored into the upper portion of a vertically positioned tubular housing so that a stream of said fluid falls through the tubular housing without touching the lateral sidewall of said upper portion of the tubular housing,

b. collecting said fluid in the bottom portion of said tubular housing which bottom portion has a diameter which is smaller than the diameter of the upper section thereof,

c. discharging said fluid from said tubular housing,

d. irradiating said falling stream of fluid with ultraviolet light transmitted through a first transparent sealed window in the upper portion of said tubular housing,

e. detecting fluorescence radiation from said irradiated falling stream of fluid through a second transparent sealed window in the upper portion of the housing, and

f. detecting the height of the column of fluid collected in the bottom of the tubular housing, and

g. injecting a gas into the upper portion of said tubular housing when the height detection of (f) indicates that the height of said fluid column is approaching the level of the sealed transparent windows.

13. The method of claim **12** wherein the gas injection of (g) is maintained at a rate so that the pressure in the tubular housing is at least 10 pounds per square inch greater than the pressure of the discharged fluid of (e).

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