

Dec. 7, 1971

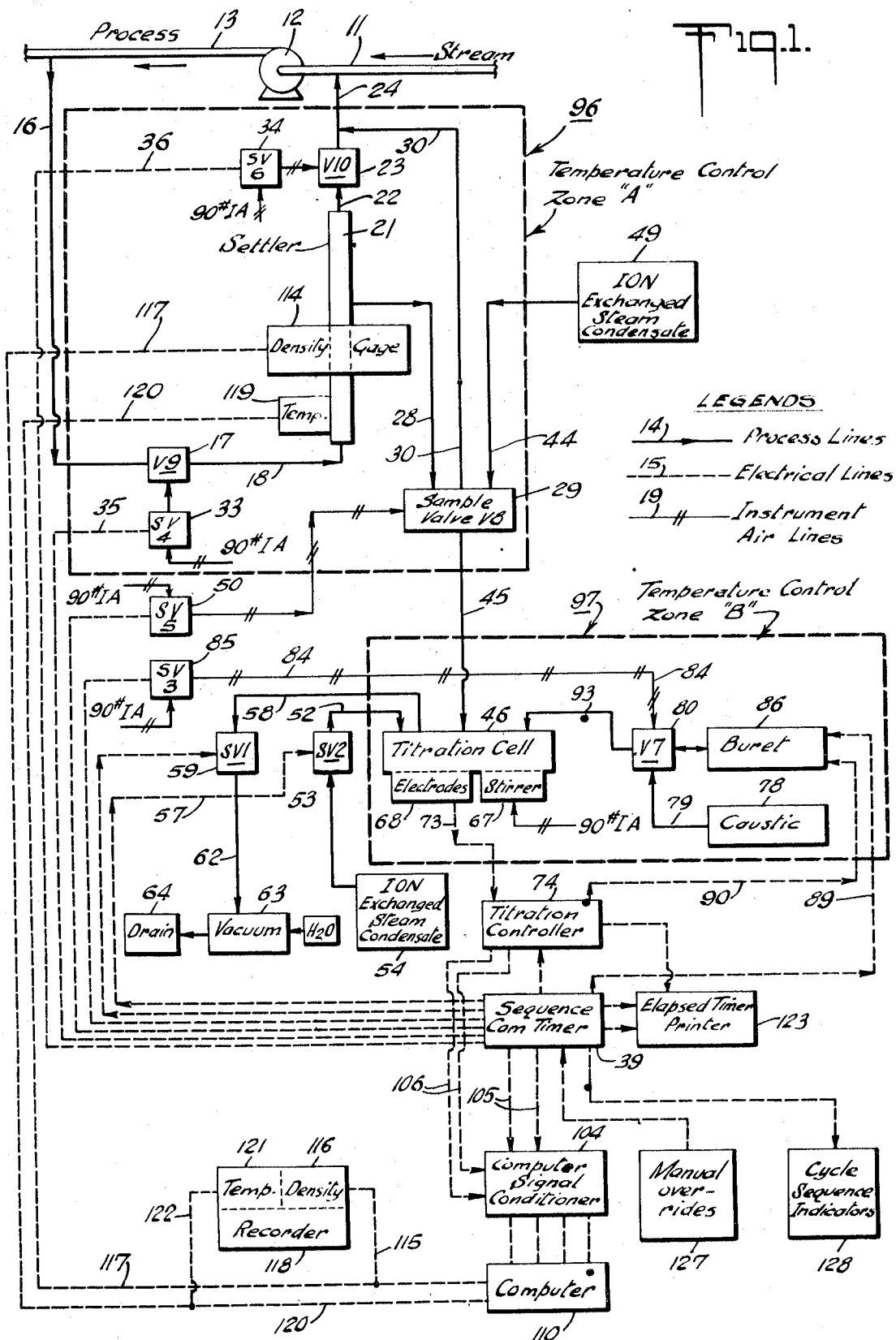
R. A. CULP., ET AL

3,625,655

ACID ANALYZER

Filed Dec. 2, 1969

4 Sheets-Sheet 1



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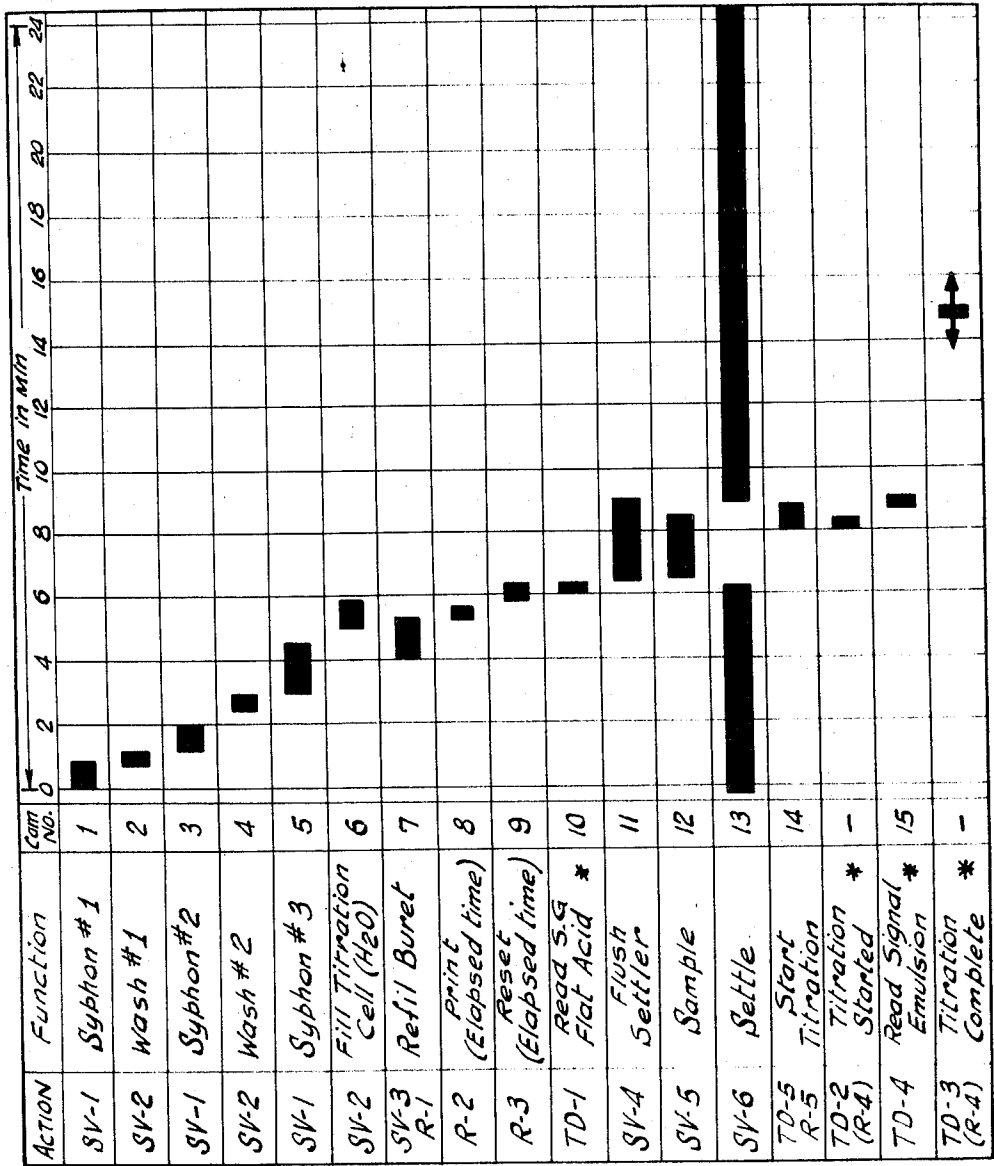
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4 Sheets-Sheet 2

NOTES:

- 1. Solenoid Valves & Relays are energized when function sequence is shown shaded
- 2. Cams #13 & #14 cam switch Contacts are N.C. in the high Cam position. All others are N.O. in the high Cam position.

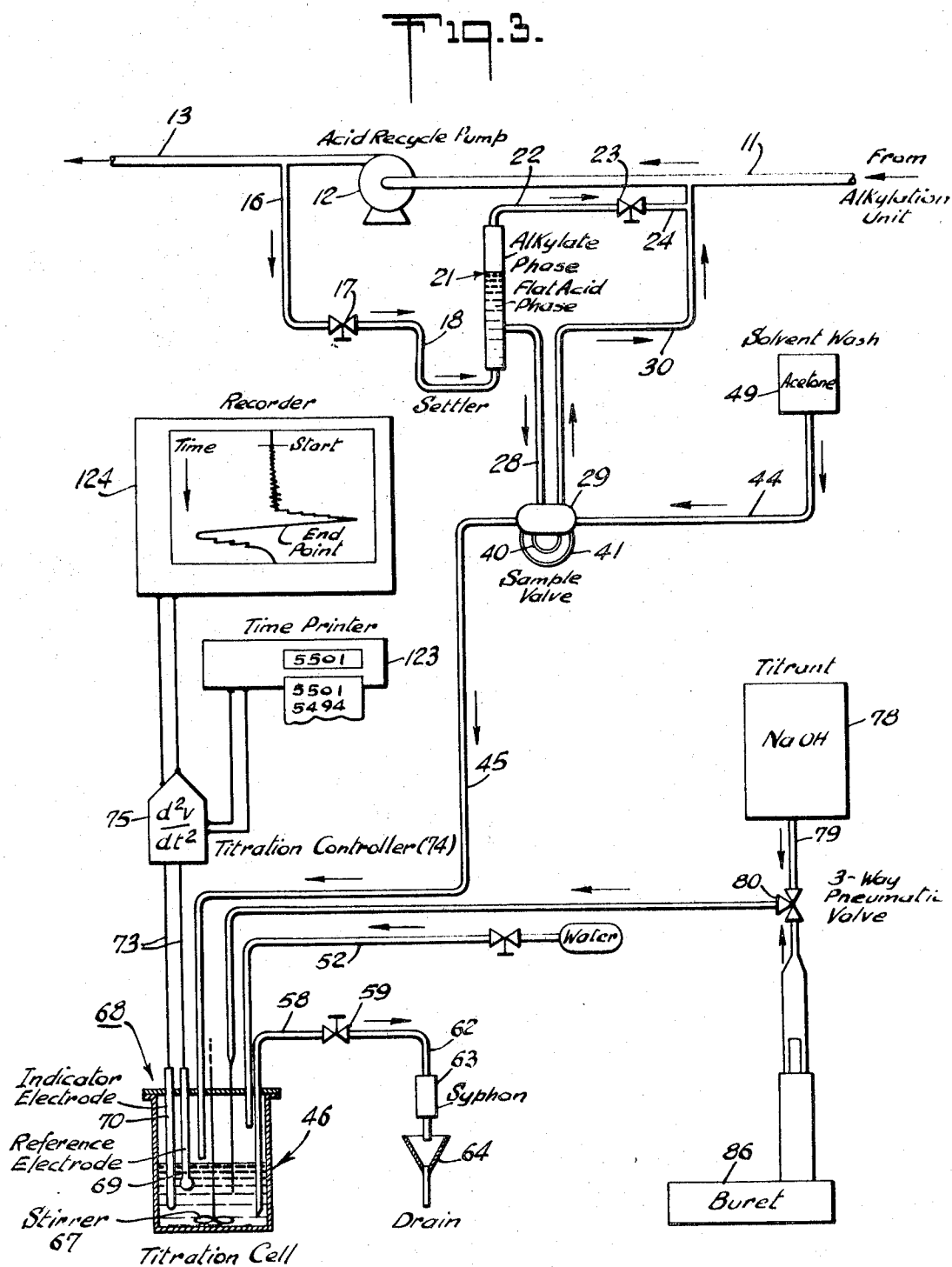
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ACID ANALYZER

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4 Sheets-Sheet 3



Dec. 7, 1971

R. A. CULP., ET AL

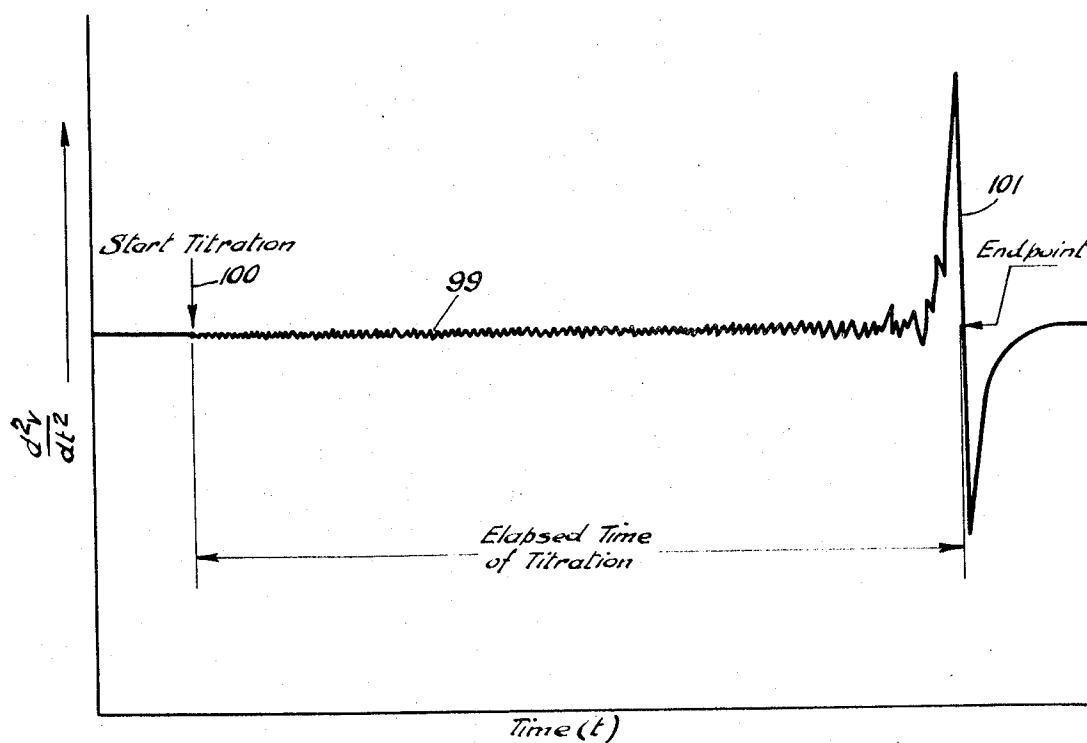
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Fig. 4.



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ACID ANALYZER

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Filed Dec. 2, 1969, Ser. No. 881,359

Int. Cl. G01n 27/10; C07c 3/14

U.S. Cl. 23—253 R

14 Claims

ABSTRACT OF THE DISCLOSURE

A system that automatically analyzes acidity or basicity of a chemical process stream periodically. The system can handle a petroleum process stream that contains an acid-hydrocarbon or base-hydrocarbon emulsion. At least some of the hydrocarbons are gaseous under normal ambient conditions. The acid, under system pressure, is settled in a vertical column and subsequently sampled. The acid or basic content of the sample is determined by a potentiometric titration.

BACKGROUND OF THE INVENTION

Field of the invention

This invention concerns a system for use in a petroleum process or other chemical process of like nature. More specifically, it concerns an analyzer that samples an emulsion of titratable material from a petroleum process which exists under super-atmospheric pressure and where the titratable material is settled out while under pressure before sampling. The system is particularly applicable to the determination of the acidity of alkylation acid.

Description of the prior art

While there have been various so-called acid analyzers available in the industry, none of those that are known have been particularly satisfactory in providing quick and accurate results that may be used in connection with the analysis and control of a petroleum process, e.g. the process known as alkylation. Such prior arrangements have not overcome a particular difficulty that relates to the fact that the acid for analysis is in the form of an emulsion under super atmospheric pressure with hydrocarbons mixed therewith and especially the fact that some of the hydrocarbons are gaseous at atmospheric pressure and ambient temperatures. Consequently, depressuring a sample of the process stream tends to cause foaming, composition changes, and other problems which have made it impossible to obtain a desirable degree of correlation between conditions in the process and titratable acidity.

SUMMARY OF THE INVENTION

Briefly, the invention relates to a combination for use in a chemical process wherein pH measurements of a constituent portion of a product stream are desired, and wherein said stream is under super-atmospheric pressure with some of the other constituents being gaseous at atmospheric pressure. The combination includes means for settling a portion of said product stream in an upstanding column under super-atmospheric pressure, and means for sampling said first-named constituent portion from said column. In the foregoing combination the last-named means comprises an auxiliary path of flow for said first-named constituent portion. The path goes from said means for settling back to said stream. The means for sampling said first-named constituent portion also comprises means for isolating and removing a sample from the said auxiliary path.

Once more, briefly, the invention comprises an acid analyzer for use with an alkylation process which in-

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cludes a recirculation stream having therein a mixture of sulfuric acid with some hydrocarbons that are liquid under super-atmospheric pressure. The said stream is recirculated through a pump.

The invention comprises in combination an upstanding column or chamber for receiving a portion of the above stream, and a first fluid passage from said stream on the outlet side of said pump to the bottom of said chamber. It also comprises a second fluid passage from the top of said chamber to said stream on the intake side of said pump, and a valve in said first fluid passage for periodically blocking flow of said stream portion to permit settling of said mixture in said chamber.

The invention also comprises an auxiliary fluid passage from the side of said chamber near the bottom of the column to said stream on the intake side of said pump, and a four-way valve having two positions and being connected to said auxiliary passage. Furthermore, it comprises a bypass conduit for permitting flow in said auxiliary passage when the said four-way valve is in one position, and a sampling conduit for permitting flow in said auxiliary passage when said four-way valve is in the other position.

Additionally, the invention comprises a titration cell, a source of neutral fluid, and conduit means for connecting said source of neutral fluid to said four-way valve and said four-way valve to said titration cell for washing out a sample when said four-way valve is in said one position.

Finally, the invention comprises means for measuring the density of the fluid in said chamber near the bottom of the column when said mixture has settled.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects and benefits of the invention will be more fully set forth below in connection with the best mode contemplated by the inventors of carrying out the invention, and in connection with which there are illustrations provided in the drawings, wherein:

FIG. 1 is a block diagram illustrating the entire system according to the invention;

FIG. 2 is a function timing chart illustrating the actions that are carried out during one full cycle of the analyzer system;

FIG. 3 is a flow diagram illustrating the various fluid handling elements that are employed in a system according to the invention; and

FIG. 4 is a graph illustrating the form of electrical output signals from one potentiometric titration run.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Ever since the advent of the petroleum process known as alkylation, there has been a need for a precise on-stream process analyzer to determine the titratable acidity of the alkylation acid. Heretofore various techniques that measure such physical properties as conductivity, specific gravity, and refractive index have been employed but these have not been successful because of the complex and varying nature of alkylation acid which made it impossible to obtain the required degree of correlation between such variables and titratable acidity. A system according to this invention has made it possible to obtain a reproducible sample and the density, and titration data required for an accurate and reliable determination of acidity.

The total system according to this invention is illustrated in FIG. 1. Also, many of the elements are schematically illustrated in FIG. 3. The process stream is a recycle flow in a sulfuric acid petroleum alkylation process consisting of an emulsion of acid and hydrocarbons.

The hydrocarbons are predominantly alkylate but some normally gaseous hydrocarbons are present. It will be observed in FIGS. 1 and 3 that the process stream flows through a pipe 11, to the suction side of an acid circulating pump 12. Then it is returned to the process from the discharge side of the pump 12 through another pipe 13.

It will be noted that the FIG. 1 illustration employs three different types of connecting lines. These are explained by the appended legend.

The analyzer process lines, which are actually pipes for carrying fluid of one sort or another, are illustrated by solid lines with arrow heads to indicate direction of flow. This is indicated by a line 14 in the legend, which is captioned "analyzer process lines."

The electrical lines, which are actually various circuits that may include electronic elements (not shown) are illustrated by dashed lines. This is indicated by a dashed line 15 in the legend.

Finally, the pneumatic lines which are actually conventional pneumatic system pipes for carrying air under superatmospheric pressure, are illustrated by solid lines that are periodically crossed by two short sloping parallel lines. This is indicated by a line 19 in the legend, which is captioned "instrument air lines."

It will be appreciated that in the actual system the required electrical power, and instrument air (pneumatic) pressure will be provided as needed. Of course, the air pressure needs to be only that required to operate the appropriate valves. In the case herein described, ninety pounds per square inch instrument air was required. Lower pressures might be satisfactory for other similar situations. Thus, input connections for pneumatic pressure will be made at various points, e.g. as indicated by the instrument air input arrows in FIG. 1 that are marked with the captions "90#1.A."

The illustrated embodiment of this invention may be described beginning with a fluid circuit for tapping off a portion of the recycled acid from an acid settler (not shown) on an alkylation unit (the "process"). Such a stream is being pumped through the pipes 11 and 13 (FIGS. 1 and 3). In describing the system, it will be noted that the block diagram of FIG. 1 may be supplemented by reference to the timing diagram illustrated in FIG. 2 as well as by the flow diagram illustrated in FIG. 3. Also, it will be observed that the same reference numbers are employed for the same elements in all three of these figures.

A portion of the recycled acid stream will tend to flow from the higher pressure pipe 13 through a flow line 16 to a pneumatically actuated valve 17, that carries the designation "V9" in FIG. 1. From valve 17 this portion of the process stream will flow through another flow line 18 to a settler 21.

Settler 21 is a vertically mounted chamber having a relatively high length to diameter ratio. It may be made of glass or steel, but if made of steel preferably it should be lined with Teflon or a similar material. It has been found that glass, Teflon and similar materials speed up the separation of acid and hydrocarbons.

The portion of the process stream that flows through settler 21 is introduced at the bottom of the settler and flows out at the top, as indicated in FIG. 3. From the settler 21 this stream portion flows through a flow line 22 and thence through another pneumatically actuated valve 23 into the main acid recycle stream, through a flow line 24. As will appear more fully below, when valve 17 is closed, flow through settler 21 is stopped and acid and hydrocarbons separate. Valve 23 is left open to reduce the settler pressure and provide means of escape for the light hydrocarbons.

At a designated time a portion of the settled, flat acid is routed from the lower portion of settler 21 through a flow line 28 to a sampling device 29. From there it is returned through another flow line 30 which joins the flow line 24 on the process stream side of valve 23 (des-

igned "V10" in FIG. 1) i.e. connects to the pipe 11. In this manner, under desired conditions (as will be described in more detail below) the flat acid from settler 21 may be caused to flow through the sample device 29 and returned to the process stream. This is done while the sample is being maintained at essentially the pressure in pipe 11. It may be desirable under some conditions to reduce the pressure in settler 21 below the pressure in pipe 11, in which case it will be necessary to discharge the flat acid to low pressure recovery facilities (not shown).

The valves 17 and 23 are pneumatically actuated. They are controlled by pneumatic pressure supplied through electrically actuated valves 33 (SV4) and 34 (SV6) respectively. It will be noted that there is an electric line 35 connected to the valve 33 and similarly another electric line 36 that is connected to the valve 34. Both of these electric control lines lead to a cam-type, sequence timer 39. This timer is conventional and may take the form of a plurality of cams, e.g. fifteen in number, which are driven by a synchronous motor (not shown) and which actuate cam follower actuated, electric switches (not shown). Such switches carry out the desired electrical controls for timing of the different functions. One complete cycle is illustrated in the timing diagram of FIG. 2.

The sampling device 29 may take various forms. Basically it is capable of segregating a predetermined volume of the titratable constituent and diverting it, along with the proper diluent, into the titration facility. In its simplest form the sampling device might consist of a four-way valve (not shown) and an outside loop (not shown) of specified volume. The valve arrangement would be such that the titratable constituent would flow normally through that loop on the way to pipe 11. Actuating that four-way valve would segregate the material contained in the loop while at the same time aligning it with a diluent supply for washing it out to the titration facility. The volume required in that loop would depend upon the strength of the titratable constituent. For alkylation acid of 80 to 98% acidity, a volume of about 0.2 to 0.3 ml. is required. For acid contents of 40 to 80%, sample volumes of 0.5 to 0.7 ml. are desirable. Varying volumes would be predetermined as required.

The required sample volume might be provided also by means of internal passages within the aforementioned four-way valve (not shown). In such case it would be necessary to provide a multiplicity of valves (not shown) with passages of different volumes to provide the flexibility desired.

A preferred form of the sampling device 29 is schematically indicated. It is adapted from a commercial valve such as that sold under the trade name Cheminert which is a dual four-way valve. That valve has a common inner slider (not shown) that may be shifted to cause simultaneous connections from two input ports (one for each four-way valve) to one of two output connections, alternatively, in each case. Each of these four-way valves has a fourth port which is connected to one of the alternative output ports, or is cut off.

The preferred arrangement of the sampling device 29 provides for completing a connection (when it is unactuated) to permit flow of acid from the settler 21 through the flow line 28 and through a sample loop 40 (FIG. 3) to the flow line 30 which carries the acid back to the process pipe 11, as described above. Then, when the sampling device 29 is actuated, its internal interport connections are shifted, as indicated above. Consequently, the flow line 28 is connected to the flow line 30 via a bypass loop 41 (FIG. 3). At the same time, the sample loop 40 has one end connected to a low line 44 with the other end connected to a flow line 45 that leads to a titration cell 46. There is a source of neutral wash fluid 49 that is then connected so as to wash out the fluid in the sample loop 40, into the titration cell 46. The neutral wash fluid may be any suitable fluid, such as the "ion-exchanged steam

condensate" indicated in FIG. 1 or the "acetone" indicated in FIG. 3. Actuation of the sampling device 29 is controlled by a pneumatic valve 50 (SV5—FIG. 1) that is controlled electrically from cam timer 39.

Titration cell 46 has conventional structure. It includes therewith another flow line 52 that leads to the cell from an electrically controlled valve 53 (designated SV2 in FIG. 1). This valve 53 controls the flow of a source of wash water 54 through the line 52. This wash water should be a neutral fluid, and consequently it is indicated in FIG. 1 as being "Ion-Exchanged Steam Condensate."

Valve 53 (SV2) is controlled electrically. This includes an electric circuit that is indicated in FIG. 1 by an electrical line 57 which leads from the sequence timer 39. This permits introduction of wash water for flushing out the titration cell 46 following each titration operation. The draining of the titration cell during such flushing procedure, is accomplished by means of a syphon arrangement. The syphon includes a flow line 58 that extends from near the bottom of the cell 46 for emptying the liquid. The line 58 goes from the titration cell 46 to a valve 59 that has connected to the other side thereof another flow line 62 which leads to a source of vacuum 63. Thus, the fluid from titration cell 46 may be syphoned out and discarded through a drain 64.

The titration cell itself is conventional. It includes a stirrer 67 for mixing the fluids in the cell during titration, and some means for determining the end point of a titration measurement.

While other means for determining the end point of a titration might be employed, it is preferred to use a potentiometric determination. This makes use of a pair of electrodes 68, one of which will be a reference electrode 69 (FIG. 3) while the other is a measuring (or indicator) electrode 70 (FIG. 3). It will be understood that these electrodes 69 and 70 together with the liquid solution in the cell 46, create an electric potential that is directly related in amplitude to the acidity pH of the fluid in the titration cell. In the system illustrated, the reference electrode is made of calomel while the measuring (or indicator) electrode is made of platinum-rhodium.

The electrical signal (potential) that is generated between the electrodes 69 and 70, is carried over a circuit that is indicated by an electrical line 73 to a titration controller 74. The latter includes an electronic amplifier 75 (FIG. 3) that has provision for amplifying the potential as developed at the electrodes 68. This is done using a second derivative circuit, in order to make accurate determination of the end point of the titration. This will be explained below in greater detail in connection with the FIG. 4 illustration.

The titration procedure, of course, involves introduction of a titrant (caustic) fluid 78 that is fed over a fluid flow line 79 to a three-way pneumatically controlled valve 80 (V7). Valve 80 is pneumatically actuated by pneumatic pressure that is introduced over a pneumatic line 84 (FIG. 1) which connects to an electrically controlled valve 85 (SV3). When valve 80 is actuated, the titrant (caustic) fluid 78 will flow through valve 80 to fill a burette 86 with titrant, which is preferably sodium hydroxide. The burette 86 is driven by a synchronous electric motor (not shown) that is controlled by signals from the cam timer 39 and the titration controller 74, via electrical lines 89 and 90 respectively, so as to start and stop a constant rate introduction of titrant from the burette 86 to the titration cell 46.

There is a flow line 93 that connects valve 80 to the titration cell 46. This flow line carries the titrant from the burette to the titration cell. It is connected except when the burette is being filled from the supply of titrant (caustic) fluid 78. Thus, when the pneumatic control valve 85 (SV3) is actuated, it causes actuation of valve 80 (V7) and this shifts the connections of this three-way valve 80 to permit titrant (caustic) 78 to be drawn into the burette 86 for filling same.

In order to have desired accuracy in the titration, the appropriate physical elements are maintained at a given constant temperature which is somewhat higher than the maximum expected ambient temperature. This is carried out in any feasible manner, e.g. by having appropriate housing 96 and 97 (FIG. 1) for the various elements along with temperature controls (not shown) as required.

It will be understood that the titration stoichiometrically determines the amount of acid in the sample solution. This involves a conventional titration operation which includes the addition of caustic in a measured amount until the solution reaches a well defined end point.

In the titration operation employed in this invention, the measurement of the quantity of caustic that is added during a titration operation is determined by having the caustic solution introduced by means of a constant rate burette. The time is then measured, from commencing to introduce the titrant until the end point (neutral condition) is reached. The beginning is easy to determine by means of a switch closure, and the exact end point is accurately determined by means of the potentiometric electrodes 69 and 70. The potential, i.e. voltage, that is created between these electrodes is measured using a second derivative electronic circuit to note the change in the rate of change of the potential that is developed. The potential which is proportional to the acidity of the solution changes rapidly near the end point and consequently the second derivative provides an accurate indication of the end point.

The foregoing explanation concerning the end point of a titration will be more fully appreciated when it is considered that the solution potential changes relative to the volume of titrant. This potential follows a rising curve which has a slope that goes from zero to a maximum and back to zero as the potential changes. Thus the end point for acidity is at the mid-point of this rising curve where the slope, i.e. the rate of change of the potential, is maximum. In other words, the electrical potential rises as the acidity decreases, and the rate of change in potential is maximum when the acidic species is depleted. Consequently, this maximum rate of change (slope) in potential marks the end point of the titration. It is most sharply defined by taking the second derivative of the potential since such derivative emphasizes the mid-point on the curve where it is a changeover from an increasing rate to a decreasing rate.

FIG. 4 illustrates a recording of the electrical signal that is obtained during a titration. Thus, in FIG. 4 there is a graph having time as the abscissa, and the second derivative of the voltage as the ordinate. A curve 99 shows the second derivative of the voltage plotted against the titration time for an actual titration. The titration time is proportional to the quantity of titrant introduced, and such time is measured by first noting the starting point of titration. This is indicated by the caption, with an arrow 100.

The output signals from the electrodes 68 (FIGS. 1 and 3) are amplified using the second derivative amplifier 75 (FIG. 3) so that the output signals produced will clearly indicate the end point of the titration. This appears in FIG. 4 as a major swing 101 on the curve 99. This has a caption "End Point" indicating the middle of the swing 101.

One advantage of the sampling and analysis system according to this invention is its adaptability to computer monitoring and control. Consequently, as is indicated in FIG. 1, there is a so-called computer signal conditioner 104 that receives electrical signals from both the sequence cam timer 39 and the titration controller 75. This is illustrated by dashed lines 105 and dashed lines 106 respectively. The output signals from this conditioner 104 are fed to a computer 110 as indicated.

An important feature of the invention is the combination with the sampling and analysis system of a density measurement made on the flat acid in the settler

21 just before sampling. This gives density data necessary to compute the titration results of acid concentration determinations since the density varies with acidity and with hydrocarbon content. Thus, there is a density gauge 114 (FIG. 1) that is incorporated physically with the settler 21, as is indicated in FIG. 1. This gauge may be one like that manufactured by the Industrial Nucleonics Corporation and marketed under the trade name AccuRay. It makes a direct density determination, electronically, of the fluid in the lower portion of settler 21.

It is also advantageous to have a reading of the temperature of the fluid in settler 21. Consequently, there is a temperature sensing element 119 (FIG. 1). This is preferably a thermocouple (not shown) so that an electrical signal output is provided which is transmitted over an electrical line 120 to the computer 110. This also is connected to a temperature section 121 of the recorder 118 over another line 122.

It may also be desirable to have a time printer 123 (FIG. 3) which is connected electrically to the titration controller via the output of the amplifier 75. This permits the time of titration to be printed for observation thereof as the cycles of operation are carried out. Also, as indicated only in FIG. 3, there may be a separate recorder 124 for making a record of the titration output signals from the amplifier 75.

Other auxiliary elements in the system may include those schematically indicated only in FIG. 1, e.g. a manual override electrical switch arrangement 127 and cycle-sequence indicators 128. These are electrically connected to the sequence cam timer 39, as indicated in FIG. 1.

OPERATION OF THE SYSTEM

In operation, the system goes through a repetitive cycle automatically. It is controlled electrically by a plurality of cams (not shown) that are part of the sequence timer 39 (FIG. 1) and are driven at a speed so as to complete one whole cycle in a predetermined time. In the illustrated instance (see FIG. 2) the time period employed is twenty-four minutes. In the alkylation process with which the system of this invention is described, the period of twenty-four minutes is ample. Shorter or longer periods may be used if desired. However, the principles of the operation are the same in any event and consequently reference may be had to the following description relating to steps of a complete cycle.

FIG. 2 illustrates the actions for a complete cycle as carried out under the control of the sequence cam timer 39 which has fifteen active cams (not shown). This is indicated in the chart of FIG. 2 where the third column is headed "Cam No." The control function is indicated under the second column headed "Function." And the valve or relay that controls the function (depending upon its actuation as determined by the cams) is listed under the first column titled "Action."

Thus, the action during a cycle of twenty-four minutes, is illustrated in FIG. 2 in the manner indicated by the appended "Notes." At the beginning of a cycle two actions are shown, one already in progress. Cam number one controls actuation of the valve SV1 (valve 59) for approximately the first minute of the cycle. At the same time, cam number thirteen is continuing to control actuation of the valve SV6 (valve 34) which in turn actuates the valve 23 (V10), holding it open.

Valve SV1 (59) opens flow lines 58 and 62 and thus actuates the syphon 63 and consequently drains the titration cell 46. Shortly before the end of that syphoning time period, number two cam will cause actuation of the valve SV2 (53) to introduce wash fluid for a short time. Next, at the end of the first wash, cam number three will again actuate the syphon 63 by opening valve SV1 (59) once more. This drains out the first wash fluid. Following a short delay, cam number four will cause actuation of valve SV2 (53) again, and this will introduce another amount of wash fluid from the source 54

of neutral fluid. At about three minutes, cam number five will cause actuation of valve SV1 (59) once more. Therefore, the titration cell 46 will be drained again. This time it is drained for a somewhat more extended period in order to be sure that it is completely empty prior to commencing a titration operation.

Before the last syphoning action just described is completed, i.e. at four minutes from the beginning of a cycle, the burette 86 is refilled. This is controlled from the cam number seven which causes actuation of the electrical circuit controls to open the pneumatic valve SV3 (85). Valve SV3 in turn causes actuation of the valve 80. Thus the burette 86 is refilled with titrant from container 78 prior to the beginning of a titration operation. It may be noted that there is a limit switch (not shown) to keep the burette from overfilling.

Before refilling of the burette is complete, cam number six causes actuation of valve SV2 (53) once more, and a predetermined amount of neutral fluid, e.g. water—in this case ion-exchanged steam condensate 54 is introduced into titration cell 46. At about the same time, cam number eight followed by cam number nine, causes actuation of relays R-2 and R-3 (both not shown) for energizing the elapsed time printer, and for resetting same thereafter so as to be ready for the next timing period (elapsed time of titration).

As indicated above, cam number thirteen is continuing to cause actuation of the pneumatic valve SV6 (34) so that the valve 23 (V10) controlled thereby is held open in order to keep process suction pressure on the fluid column in the settler 21 all during the settling time. At the very end of the settling time, i.e. beginning at six minutes of the illustrated cycle, cam number ten causes actuation of a time delay relay TD-1 (not shown) for a short time. This provides a density reading at the end of the settling period. Consequently, this reading pertains to the flat acid which is standing in the settler column 21. The reading is determined by the density gauge 114.

Next, and right after the valve SV6 (34) which controls valve 23 (V10), is closed, i.e. de-energized (end of the shaded bar opposite cam number thirteen); cams number eleven and number twelve, in that order, cause actuation of valves SV4 (valve 33) and SV5 (valve 50) respectively. Consequently, right after settler column outlet valve 23 is closed, the inlet valve 17 is opened to apply pump discharge pressure from the process stream. This causes sample loop 40 of sampling device 29 to be filled with acid that has been settled in settler 21. Immediately thereafter sampling device 29 is actuated to cause wash flow through sample loop 40.

As explained above, actuation of the sampling device 29 (controlled by valve SV5 (50)) shifts the sample loop 40 into connection with the source 49 of wash fluid, and the titration cell 46. Therefore, the sample is washed into the cell during the time when cam number twelve causes that actuation. At the same time, in preparation for the next sample, settler 21 is flushed by the application of pressure from the pressure side of the process stream in pipe 13. Such pressure comes through valve 17 (V9) which is controlled by the pneumatic valve SV4 (33).

The flushing of the settler 21, at first only goes through the bypass 41 of the sample valve 29 until at about seven and one half minutes in the total cycle when the cam thirteen causes the valve SV6 (34) to be opened again, which in turn opens the valve 23 (V10). Thereafter, the flushing continues through the whole settler column in parallel with the sample valve, until at about nine minutes in the cycle when cam number eleven causes valve 17 (V9) under control of valve SV4 (33) to be closed again. This commences the next settling.

In the meantime, near the end of the time when the sample valve 29 under control of valve SV5 (50) is shifted, cam number fourteen actuates a time delay relay (not shown) and another relay (not shown). This starts

the introduction of titrant (start of titration) since the sample is fully washed into the titration cell and is being mixed continuously. Also, at the same instant that the introduction of titrant starts, titration controller 74 operates a relay (not shown) that generates a "titration started" signal which is indicated in the next line below in the FIG. 2 diagram. This signal is sent to computer 110, as well as feeding a parallel signal to printer 123. The titration runs its course under control of the separate titration controller 74 (FIG. 1) as has been described above. The signals from the operation are applied to the computer, as already indicated.

Although it has no direct relation to the determination of acidity, a cam number fifteen may be used to activate a reading of the density of the emulsion in the settler column 21. It will be noted that this reading is taken near the end of the time when the inlet valve 17 (V9) controlled by valve SV4 (33) for the settler column 21, is open. This is when fresh emulsion from the process stream is flowing through the settler in preparation for the next sampling to be titrated. This reading is useful to estimate the ratio of acid to hydrocarbon in the process stream.

As indicated on the last line of the FIG. 2 diagram, there is a "titration complete" signal that is generated in the titration controller 74. This signal is sent to the computer 110, as well as feeding a parallel signal to the printer 123.

An example of a given calculation for determining the acidity following the completion of a titration follows:

Weight percent H_2SO_4

$$= \frac{\text{Volume of caustic} \times \text{Normality of caustic} \times \text{Milliequivalent weight of } H_2SO_4}{\text{Weight of acid sample}} \times 100$$

where:

(1) Volume of caustic = elapsed time $\times$ rate of caustic addition

$$= \text{Time (sec.)} \times 1/12 \text{ (ml. sec.)}$$

(2) Normality of caustic = 0.200 (meq./ml.)

(3) Milliequivalent weight of H_2SO_4 = 0.04904 (grams/meq.)

(4) Weight of acid sample = Volume of acid $\times$ specific gravity
 $= 0.200 \text{ (ml.)} \times \text{specific gravity (gram/ml.)}$

Weight percent H_2SO_4

$$\begin{aligned} & \frac{\text{Time (sec.)} \times 1/12 \text{ (ml./sec.)} \times 0.200 \text{ (meq./ml.)} \times 0.04904 \text{ (grams/meq.)}}{0.200 \text{ (ml.)} \times \text{Specific gravity (grams/ml.)}} \times 100 \\ &= \frac{0.04904 \times 100}{12} \frac{\text{Time in seconds}}{\text{Specific gravity}} \end{aligned}$$

Sample calculation

Where:

(1) Elapsed time of titration = 401.27 sec.

(2) Specific gravity = 1.7391

Therefore:

$$\begin{aligned} \text{Wt. percent } H_2SO_4 &= \frac{0.04904 \times 100}{12} \times \frac{401.27}{1.7391} \\ &= 94.29 \end{aligned}$$

It is to be noted particularly that the operation of a sampling system according to this invention, permits the periodic sampling of a flat acid sample from an alkylation process stream, without running into any of the difficulties that in the past have prevented correlation of sampling variables with titratable acidity. Such difficulties relate to sampling of a stream of fluid that exists in the process under superatmospheric pressure, and that contains an emulsion of an acid with hydrocarbons, some of

which are gaseous at atmospheric pressure and normal ambient temperature.

While the foregoing description has been made in considerable detail in accordance with the applicable statutes, it is not to be taken as in any way limiting the invention but merely as being descriptive thereof.

We claim:

1. Apparatus for use in a chemical process wherein acidity and basicity pH measurements of a constituent portion of a product stream are desired and wherein said stream is under super-atmospheric pressure with some of the other constituents being gaseous at atmospheric pressure, the combination of

means for settling a portion of said product stream in an upstanding column under super-atmospheric pressure, and

means for sampling said first-named constituent portion from said column,

wherein

said last-named sampling means comprises an auxiliary path of flow for said first-named constituent portion, from said means for settling back to said stream, and means for isolating and removing a sample from said auxiliary path.

2. The invention according to claim 1, wherein said means for isolating and removing includes

alternative paths in said auxiliary path of flow means for connecting a wash fluid to one of said alternative paths, and

valve means for switching said auxiliary path of flow from one to the other of said alternative paths.

3. The invention according to claim 2 further including a titration cell.

4. The invention according to claim 2 wherein said product stream flows through a pump that increases the amount of pressure, and

further including a path of flow from said product stream on the discharge side of said pump to the bottom of said upstanding column.

5. The invention according to claim 4 further including valve means in said last-named path of flow.

6. Apparatus for use in a chemical process wherein acidity or basicity pH measurements of a constituent portion of a product stream are desired and wherein said stream flows through a pump that increases the amplitude of super-atmospheric pressure on said stream with at least some of the other constituent portions being gaseous at atmospheric pressure, the combination of

an upstanding column or chamber having interior walls of material that is impervious to the constituents of said stream,

a first path of flow from the discharge side of said pump to the bottom of said chamber including a first valve therein for periodically blocking said first path,

a second path of flow from the top of said chamber to the intake side of said pump including a second valve therein for periodically blocking said second path,

an auxiliary path of flow from in between the top and bottom of said chamber to the intake side of said pump including a sampling valve for periodically diverting a sample of said constituent following a settling thereof in said chamber, and

a titration cell for receiving the said constituent sample in order to make the desired pH measurement of acidity or basicity.

7. An acid analyzer for use with a petroleum process including a process stream having therein an emulsion of an acid with some hydrocarbons that are liquid under super-atmospheric pressure, comprising in combination

means for passing a portion of said stream through an upstanding column under said super-atmospheric pressure,

means for periodically blocking flow of said stream

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portion in said column to permit said emulsion to separate in said column,
means for sampling and titrating some of the settled acid from said column, and
means for measuring the density of the settled acid in

8. An acid analyzer according to claim 7 wherein said petroleum process is an alkylation process and said stream is a recirculation of an acid hydrocarbon mixture through a pump.

9. An acid analyzer according to claim 8 wherein said means for passing a portion of said stream, comprises

a first fluid passage from the stream on the outlet side of said pump to the bottom of said upstanding column and

a second fluid passage from the top of said column to the stream on the intake side of said pump.

10. An acid analyzer according to claim 9 wherein said means for periodically blocking flow, comprises a valve in said first fluid passage.

11. An acid analyzer according to claim 10 wherein said means for sampling and titrating, comprises

an auxiliary fluid passage from in between the top and bottom of said column to the stream on the intake side of said pump, and

means for diverting a sample of the settled acid into a titration cell.

12. An acid analyzer according to claim 11 wherein said means for diverting a sample comprises

valve means associated with said auxiliary fluid passage,

a bypass conduit for permitting flow in said auxiliary passage when said valve means is actuated to one position,

a sampling conduit for permitting flow in said auxiliary passage when said valve means is actuated to another position, and

means for depositing a sample from said sampling conduit into said titration cell.

13. An acid analyzer according to claim 12 wherein said valve means associated comprises

a four-way valve, and

means for connecting said bypass conduit and said sampling conduit thereto, and

wherein said means for depositing comprises

a source of neutral fluid, and

means for connecting said source to said titration cell via said four-way valve.

14. An acid analyzer for use with an alkylation process including a recirculation stream having a mixture of sulfuric acid with some hydrocarbons that are liquid under

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super-atmospheric pressure, said stream being recirculated through a pump, comprising in combination.

an upstanding column or chamber for receiving a portion of said stream,

a first fluid passage from said stream on the outlet side of said pump to the bottom of said chamber,
a second fluid passage from the top of said chamber to said stream on the intake side of said pump,

a valve in said first fluid passage for periodically blocking flow of said stream portion to permit settling of said mixture in said chamber,

an auxiliary fluid passage from the side of said chamber near the bottom of the column to said stream on the intake side of said pump,

a four-way valve having two positions and being connected to said auxiliary passage,

a bypass conduit for permitting flow in said auxiliary passage when said four-way valve is in one position,

a sampling conduit for permitting flow in said auxiliary passage when said four-way valve is in the other position,

a titration cell,

a source of neutral fluid,

conduit means for connecting said source of neutral fluid to said four-way valve and said four-way valve to said titration cell for washing out a sample when said four-way valve is in said one position, and

means for measuring the density of the fluid in said chamber near the bottom of the column when said mixture has settled.

References Cited

UNITED STATES PATENTS

2,592,063	4/1952	Persyn, Jr.	23—253
2,977,199	3/1961	Quittner	23—253 X
2,989,377	6/1961	Leisey	23—253 X
3,173,969	3/1965	Kapff	23—253 X

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U.S. Cl. X.R.

23—230 R, 230 A, 253A; 204—195; 260—683.58, 683.59; 324—30 R

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,625,655 Dated December 7, 1971

Inventor(s) Robert A. Culp, Jr., and Robert E. Franke

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 10, line 27, (in Claim 2, third line)
please cancel "means);
line 28, (at the beginning of the line)
before "for" insert (with single
indent) -- means --

Signed and sealed this 30th day of May 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents