Feb. 6, 1951 R. W. PACHALY 2,540,377

APPARATUS FOR DETERMINING VAPOR PRESSURE

Filed March 25, 1947 2 Sheets-Sheet 1

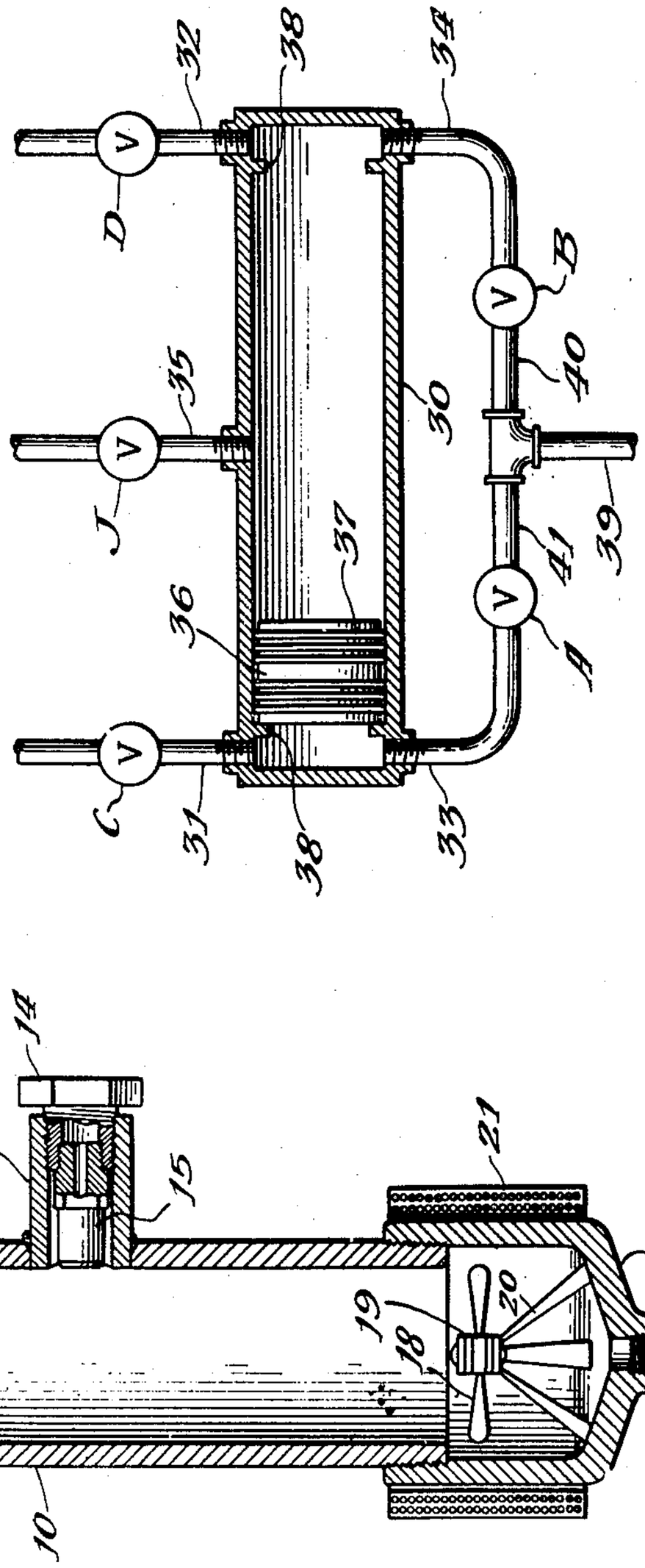

FIG. 2.

FIG. 1.

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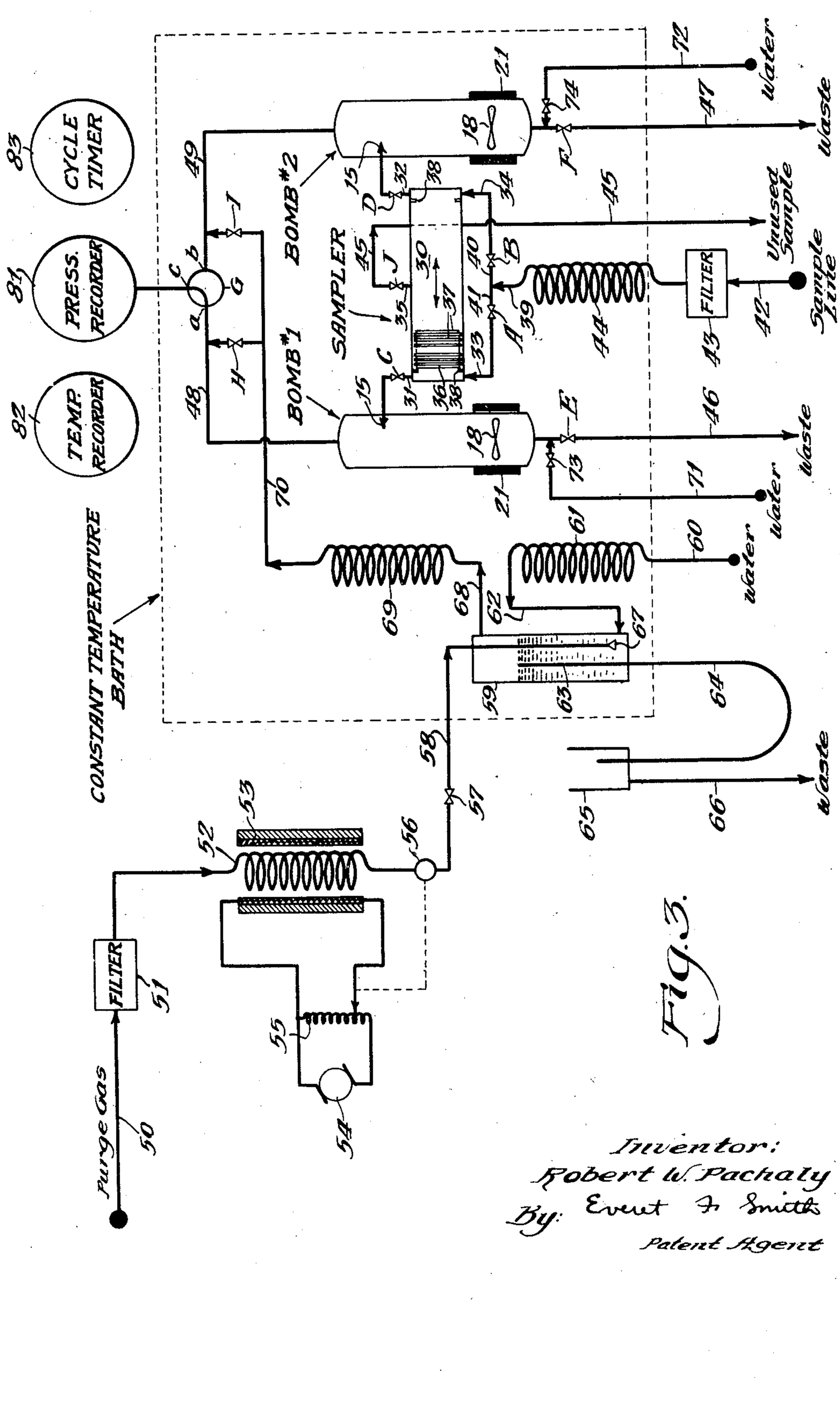

Fig. 3.

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APPARATUS FOR DETERMINING VAPOR PRESSURE

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1 Claim. (Cl. 73—29)

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This invention relates to the determination of the vapor pressure of liquids. More particularly, it relates to an apparatus and a method for determining the pressure developed over the surface of a liquid in a closed container.

The apparatus of my invention broadly comprises a multiplicity of chambers, equipped with suitable lines, valves, temperature-regulating means, and pressure-measuring means; and in combination therewith, a novel device for sampling a liquid stream and for conveniently and accurately measuring and introducing samples of the liquid into the pressure-measuring chambers.

The object of my invention is to provide an apparatus and a method for rapidly and conveniently determining the vapor pressure of liquids, and in particular for determining the so-called "Reid vapor pressure" of naphthas, gasolines, and liquefied petroleum gases.

The specifications under which gasoline is ordinarily sold require that its vapor pressure fall within a relatively narrow range. This requirement is of great importance to the consumer, since, if the vapor pressure is too high, the carburetor of his automobile will tend to vapor-lock, whereas if the vapor pressure is too low, the gasoline will have poor starting characteristics. In the production of gasoline, a number of hydrocarbon streams having various characteristics are ordinarily blended by the refiner, in order to produce a fuel having the desired properties with respect to vapor pressure, anti-knock rating, and the like, and in order to effect the most economical use of the available raw materials. The refiner may find it advantageous, for example, to incorporate in the gasoline as high a proportion of the relatively cheap low-boiling hydrocarbons as possible; however, the proportion of such low-boiling hydrocarbons must be limited so that the allowable vapor pressure of the finished product is not exceeded. It will be apparent, therefore, that the refiner cannot safely approach nearer to the maximum allowable vapor pressure than the probable error of the method used for determining the vapor pressure of the finished product.

Gasoline is now marketed under specifications based on the Reid method for vapor-pressure determination (ASTM D 323-42), which was originally devised in 1930. This method employs an apparatus comprising an air chamber, a Bourdon-type pressure gage, and a liquid sample chamber. The air chamber has a diameter of approximately 2 1/16" and a length of 10" (inside

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dimensions). Openings with suitable external connections are provided at each end, and the inner surfaces at the ends are sloped to permit complete drainage through the connection elements. The liquid sample chamber has the same inside diameter and a length sufficient to provide an overall vapor-to-liquid ratio of 3.8 to 4.2 when attached to the air chamber. Both the pressure gage and the liquid sample chamber are supplied with male screw connections for attachment to the air chamber. In determining vapor pressure with this apparatus, the air chamber is first carefully purged and rised with water, a film of water being left behind so that during the test the liquid sample and vapor space will be saturated with water, and the pressure gage is next screwed into place. The sample liquid, having first been chilled, is then introduced into the sample chamber, and the sample chamber is screwed into the air chamber. The assembled apparatus is shaken vigorously and immersed in a water bath maintained at a constant temperature (for gasoline, 100 plus or minus 0.2° F.) until the pressure reaches equilibrium.

The foregoing method provides reasonably accurate results, if due care is taken to avoid leaks from sample containers and from the test equipment, to standardize equipment size, and to make various corrections, such as for the temperature of the air initially present in the bomb and for the temperature of the sample. However, it is a comparatively slow procedure, requiring around a half hour or more for each determination, even when carried out by a skilled operator, and is subject to the usual human errors of manipulation. Moreover, special facilities must be provided for taking samples of the gasoline stream, and the samples must be refrigerated until such time as the vapor-pressure determination can be made. From the point of view of the refiner, however, the most serious drawback of the method is its failure to provide information on the basis of which the blending operation itself can be satisfactorily regulated. In ordinary blending operations, as much as 5,000 barrels of gasoline per hour may be produced, during which the composition of the streams being blended may alter materially, thus influencing the properties of the product. If the operator must wait a half hour or longer after any change in the operating conditions before he can determine the effect of the change on the product, he obviously may be unable to prevent the occurrence of substantial deviations from the prescribed range of vapor pressure during such time.

Efforts have been made to devise equipment for measuring the so-called "true vapor pressure" of the blended gasoline by continuously passing a side-stream of the blend into an evaporating cup, and measuring the pressure developed therein. This technique can be employed successfully for measuring the vapor pressure of a liquid which contains no dissolved non-condensible gases; however, virtually all gasoline streams contain dissolved air and lower hydrocarbons, which come out of solution and accumulate in the evaporating cup, eventually rendering the device completely inoperative. For this reason, true vapor pressure apparatus has not proved successful in the regulation of gasoline-blending operations.

I have now devised a new apparatus wherewith a stream of gasoline or other liquid may be sampled, and the vapor pressure of the sample may be determined conveniently and rapidly by introduction into one of a multiplicity of vessels, such as Reid-type bombs, the sample being measured and injected into the vessel by means of a novel sampling device, and the equipment being operated manually or automatically as desired.

The apparatus of my invention comprises two or more pressure-measuring vessels, preferably of the general type and size employed in the original Reid test, a sample measuring and feeding device, to be designated "sampler" and to be described more fully hereinafter, suitable valves for controlling flows, devices for measuring and optionally for recording temperatures and pressures, means for maintaining the apparatus at constant temperature, means for purging the pressure-measuring vessels free of vapors prior to conducting a test, means for supplying water to the sample in slight excess over the quantity required to saturate the liquid and the vapor space within the test vessel, and optionally means for automatically controlling the operation of the equipment according to a prearranged cycle.

The pressure-measuring vessels employed in my apparatus should preferably be of substantially the same dimensions as the standard Reid bombs, particularly with respect to inside diameter, total volume, and vapor-to-liquid ratio, so that the pressure readings obtained are approximately the same as those obtained by the Reid method. I therefore choose ordinarily to construct the vessels with an inside diameter of approximately $2\frac{1}{16}''$ and a total volume of approximately 41.75 cubic inches. If, then, a sample measuring 8.35 cubic inches is introduced into this vessel, the ratio of vapor to liquid will be approximately 4.0, as required in the Reid method. It will be understood, however, that wide departures may be made from the specified dimensions and from the designated sample volume without substantially diminishing the utility of my invention, since apparatus embodying such departures may readily be calibrated against standard Reid-test equipment.

Various techniques may be employed for injecting the liquid sample into the pressure-test vessel. For example, I may choose to introduce the liquid into the bottom of the vessel, according to the usual Reid-test technique. Or, I may introduce the liquid into the top of the vessel, allowing it to fall downward through the air and to wet the walls, the attainment of equilibrium conditions being facilitated thereby. Preferably, however, I insert a conventional spray nozzle through the wall of the pressure-test vessel, and spray the liquid sample into the vessel through the nozzle. As a result of thus intimately mixing the liquid sample with the air in the test vessel, the equilibrium vapor pressure is rapidly attained, and the rate at which the tests can be carried out is materially increased.

In order to expedite the attainment of equilibrium within the pressure-measuring vessel, it is desirable to provide means for agitating the contents thereof. For this purpose, it is convenient to introduce an agitator into the vessel through a suitable packing gland. Alternatively and preferably, however, I may introduce an agitator blade of magnetic material into the lower part of the pressure vessel, supporting the blade on a suitable bearing, and energize the blade with a rotating magnetic field, supplied by a coil outside of the vessel walls. In this case, the pressure vessel should be constructed of non-magnetic materials, such as stainless steel, copper, brass, or everdur, in order to interfere as little as possible with the magnetic field.

Fig. 1 represents one embodiment of a vapor pressure measuring vessel.

Fig. 2 represents one embodiment of the sampler used.

Fig. 3 is a diagrammatic view of typical process apparatus utilizing the vapor pressure bomb and sampler of Figs. 1 and 2.

One embodiment of the pressure-measuring vessel used in my invention is illustrated by Figure 1. Element 10 therein is a cylindrical brass vessel, having an open, externally threaded lower end, and a closed upper end 11 with an internally threaded connector port 12. In the longitudinal wall of element 10 is brazed a nipple 13, internally threaded at the outer end; and into pipe 13 is screwed a bushing 14, carrying spray nozzle 15. The liquid to be tested is introduced into the vessel through a line (not shown) screwed into the outer opening of bushing. 14. To the lower end of element 10 is screwed a cup-shaped brass member 16 having an internally threaded connection 17 at the lower end, and carrying a steel agitator blade 18 attached to bearing 19 supported on tripod 20. The agitator blade 18 is driven indirectly by a rotating magnetic field set up by a coil 21 surrounding element 16. Pyrometer wells (not shown) may be provided in the liquid and vapor spaces of the pressure-measuring vessel for the accommodation of suitable temperature-measuring devices, such as thermocouples or resistance elements.

The sampler employed in my apparatus comprises means for isolating a quantity of a stream of liquid, and means for injecting a standard volume of the isolated liquid into the pressure-test vessel, said means being operated by positive pressure of the stream of liquid from which the sample is segregated. The sampler is a hollow, elongated vessel, preferably not necessarily cylindrical in cross-section, and preferably not necessarily having its long axis in a horizontal position. One or more openings are provided in each of the end portions of the vessel for ingress and egress of the liquid to be sampled; and in the central portion of the longitudinal wall of the vessel another opening is provided as an exit, in order to permit a stream of the liquid that is to be tested to flow through the sampler continuously, except during the intervals

when a sample has been isolated within the sampler and is being introduced into a pressure-test vessel. Within the sampler vessel is a movable piston, which should be equipped with sealing means, such as piston rings, fitted accurately to the inner walls of the sampler vessel, the vessel being divided thereby into two distinct portions.

In the above description, the term "end portions of the vessel" is to be understood as including the end walls and also such portions of the ends of the longitudinal walls as are not blocked or sealed off by the piston at its nearest approach to the ends of the vessel. Similarly, the term "central portion of the longitudinal wall" is to be understood as including all of the central portion of the longitudinal wall not blocked or sealed off by the piston at its nearest approach to both ends of the vessel.

One embodiment of the sampler employed in my apparatus is illustrated by Figure 2. In the figure, element **30** is a cylindrical vessel, closed at each end, and equipped with upper openings **31** and **32** and lower openings **33** and **34** at each end, and with one opening **35** in the upper central portion of the cylinder wall. Each of the openings is provided with a valve, A, B, C, D, and J. Within the cylinder is a freely moving piston **36**, having two sets of piston rings **37** which in combination effectively divide the cylinder into two portions. The travel of the piston is limited by stops **38** so that the piston cannot block the openings in the end portions of the cylinder. In normal operation, the stream of liquid to be tested is supplied to the sampler at a pressure sufficient to move piston **36** and to overcome the frictional resistance of lines **31** and **32** leading from the sampler into the pressure-measuring vessels (not shown). The sample stream, supplied through line **39**, enters the sampler cylinder alternatively through valve A or valve B and the associated lines. If, for example, the piston is at rest at the left end of the cylinder, as illustrated, then valves A, C, and D are normally closed, while valves B and J are open, permitting the liquid stream to flow through lines **40**, **34**, and **35**, and to be discarded or otherwise disposed of through valve J. The liquid to the right of piston **36** is therefore a representative sample of the liquid entering through line **39**. When it is desired to introduce this sample into a pressure-test vessel, then valves J and B are successively or simultaneously closed, and thereafter valves A and D are successively or simultaneously opened. The pressure existing in sample line **39** is thereby applied to the left face of piston **36**, driving it to the right and forcing the sample through line **32** and valve D into the pressure-test vessel (not illustrated). After the piston has reached the right end of the cylinder, valve D is closed, thereby isolating the pressure-test vessel, and valve J is opened. The liquid stream from line **39** then flows continuously through line **41**, valve A, line **33**, and the left-hand portion of the sampler cylinder, and emerges through line **35** and valve J. Thereupon, by reversing the procedure outlined above, another sample may be isolated and ejected through line **31** and valve C into a pressure-test vessel.

Numerous modifications may be made in the sampling device described above without departing from the mode of operation upon which the superiority of my invention rests. For example, a single opening may be provided in each end of vessel **30**, instead of the two openings shown in Figure 2, and the pair of lines connected to each end may then be joined by means of a T to the single opening. Piston **36** may be constructed with conical, hemispherical, or otherwise modified ends, and the internal shape of the ends of vessel **30** may be modified substantially to fit, so that a minimum of liquid is left undischarged at the end of the piston's stroke. It will be apparent, however, that at the nearest point of approach of the piston to either end of vessel **30**, it should not block the openings in that end in such a way as to prevent the subsequent introduction of the liquid stream from line **39** therein. Piston **36** may have a length as great as the distance between stop **38** and the nearest edge of outlet **35**, so that the entering stream of sample liquid effectively sweeps the free portion of vessel **30** and renders its contents a truly representative sample of the sample stream at all times. Outlet **35** may comprise a multiplicity of openings, if desired, each provided with suitable control valve.

It will be apparent to those skilled in the art that the sampling device illustrated above is greatly superior to the means employed in the prior art for sampling liquid streams. My apparatus avoids the necessity for taking chilled samples, for storing the samples, and for transferring samples from isolated vessels into the test equipment. In avoiding these operations, my invention entirely prevents volatilization losses from samples—probably the most important cause of error in the prior-art methods. Moreover, the use of my apparatus makes it unnecessary to employ correction factors or constants to allow for errors arising from the use of chilled samples.

My combination of sampler and pressure-test vessels is most conveniently and satisfactorily operated in conjunction with certain auxiliary equipment. It is desirable, for example, to place the entire test unit in a constant-temperature bath, suitably of conventional design, in order to obtain dependable results. Such a bath should comprise pyrometric means, a temperature-control device, a heating element, a cooling coil, an inlet for the heat-transfer medium (suitably water or oil), an overflow pipe, and a drain line. The pressure gauge need not be placed in the constant-temperature bath; however, its temperature should not differ by any wide margin from the temperature of the rest of the equipment. The liquid stream entering the equipment should preferably be heated or cooled to the temperature of the bath before entering the sampler. This temperature adjustment may be carried out by passing the stream through a heat interchanger in the constant-temperature bath itself, suitably a coil of copper tubing having, for example, a total length of around 25 feet, an outside diameter of ¼", and an inside diameter of $\frac{3}{16}$". Before each sample is run, the pressure-test vessel should be purged substantially free of vapors and residual liquid from the previous sample. For this purpose, a primary purge with water may be used, followed by any gas that is substantially insoluble in the liquid to be tested. The water purge is not essential, however, and may be omitted. Air is a convenient purge gas for use in tests on gasoline. The purge gas stream may be filtered and preheated externally, and may then be saturated with water by any convenient means, if it is desired to determine the vapor pressure of the sample under water-saturated conditions. Subsequently, the purge gas stream may be passed through a suitable heat exchanger coil immersed in the constant-

temperature bath, in the manner used for preheating the liquid sample stream. The pressure gauge should preferably be of the recording type, to facilitate the determination of the equilibrium pressure, and to provide a convenient pressure-vs.-time record of the liquid stream. It is desirable also to provide a suitable temperature recorder and associated pyrometric equipment to keep a concurrent record of the temperatures of the bath, the preheated sample stream, the liquid and vapor zones in the pressure-test vessel, and the preheated purge-gas stream, since the accuracy of the results depends very closely on the accuracy of temperature control. The various valves required in the apparatus may be of the manually operated type; however, the apparatus may be made virtually self-operating by installing solenoid-operated or mechanically operated valves and providing a cycle-timer of conventional design to open and close the valves according to a prearranged schedule.

My invention will be more readily understood from the following example, to be read in conjunction with Figure 3.

EXAMPLE

In Figure 3, bombs **1** and **2** are pressure-test vessels, equipped with spray nozzles **15**, stirrers **18** operated magnetically by coils **21**, and a sampler device **30** as described above. In the following description, a vapor-pressure test will be assumed to be in progress in bomb **1**, and bomb **2** will be assumed to be undergoing an air-purge in preparation for a succeeding test. Under these conditions, the positions of the valves are as follows: valves A, C, D, E, and H are closed; valves B, F, I, and J are open; and multi-position valve G is open in direction *a*—*c* only. The liquid stream which is to be tested enters the equipment through line **42**, filter **43**, heat-interchanger coil **44**, line **39**, line **40**, valve B, line **34**, and sampler **30**. From the sampler, the liquid stream emerges through line **35**, valve J, and line **45**, from which the unused sample is disposed of as desired.

Meanwhile, the liquid in bomb **1** is vigorously stirred by agitator **18** until the pressure reaches equilibrium, as indicated on pressure recorder **81**, and until the temperature within the bomb approximates that of the constant-temperature bath, both temperatures being shown on recorder **82**. As soon as equilibrium is reached, the test has been completed, and the sample is discarded; afterwards, the bomb is purged and prepared for another test. To discontinue the test in bomb **1** and to start a test in bomb **2**, the following sequence of valve changes is required:

Open valves E and H. This applies air pressure to the top of the liquid in bomb **1** and assists in ejecting it through valve E and line **46**. As soon as the liquid has been expelled, shift valve G to the open position in direction *b*—*c* only, thereby connecting pressure recorder **81** to bomb **2**. Close valve I to disconnect the air supply from bomb **2**. Close valves J and B; this isolates within the sampler the new sample of liquid to be tested. Then open valve A; this applies the pressure of the sample line to the left side of piston **36**. Close valve F; this seals bomb **2**, filled with air at one atmosphere and at the temperature of the bath. Open valve D; this permits the piston **36** to move to the right and spray the liquid sample into bomb **2** through spray nozzle **15**. As soon as all of the sample has been introduced into the bomb, close valve D. Then open valve J. The equipment is now in the reverse of its initial position: a pressure test is now being carried on in bomb **2**, bomb **1** is being purged for the succeeding test, and a sample stream is flowing through the left side of sampler **30**. The following tables will clarify the valve settings existing in the initial and final stages outlined above, and the valve changes necessary in shifting from one test position to the other:

TABLE 1

Valve settings

Valve	Bomb 1 operating, Bomb 2 purging	Bomb 2 operating, Bomb 1 purging
A	Closed	Open.
B	Open	Closed.
C	Closed	Do.
D	do	Do.
E	do	Open.
F	Open	Closed.
G	*a*—*c*	*b*—*c*.
H	Closed	Open.
I	Open	Closed.
J	do	Open.

TABLE 2

Valve changes

Operation No.	Bomb 1 operating, Bomb 2 purging; to reverse:	Bomb 2 operating, Bomb 1 purging; to reverse:
1	Open E, H	Open F, I.
2	Change G to *b*—*c*.	Change G to *a*—*c*.
3	Close I	Close H.
4	Close J, B	Close J, A.
5	Open A	Open B.
6	Close F	Close E.
7	Open D	Open C.
8	Close D	Close C.
9	Open J	Open J.

Air or other suitable gas for purging the bombs is supplied through line **50**, filter **51**, preheater coil **52**, and flow-control valve **57**. The preheater coil **52** is heated by furnace **53**, to which electrical energy is supplied from source **54** through autotransformer **55**, regulated by pyrometric means **56**. The gas emerging from flow control valve **57** passes through line **58** into water-saturator **59**, immersed in the constant-temperature bath. A column of water is maintained within vessel **59** by supplying water thereto through line **60**, heater interchanger coil **61**, and line **62**, and allowing the excess to overflow through overflow pipe **63**, seal **64**, overflow box **65**, and waste line **66**. The purge gas is broken up by disperser **67** and contacted with the water column. Afterwards, the purge gas, now saturated with water, passes out of the saturator through line **68**, heat interchanger coil **69**, and line **70**, and is supplied to the pressure-test vessels through valves H and I and lines **48** and **49**.

Water in slight excess over the quantity required to saturate the liquid sample may be supplied in a variety of ways. For example, a small quantity may be added continuously to the sample stream flowing to the sampler by means of a proportioning pump. Or, preferably, a small quantity of water may be injected into the bomb concurrently with the sample via lines **71** or **72** and check valves **73** or **74**.

It will be apparent that multiple-direction valves, like valve G, may be substituted for single-direction valves at a number of points. For ex-

ample, valves A and B may be replaced with a two-way valve.

All of the valves used in the equipment are preferably of the solenoid type, and are actuated by a cycle timer 83 of conventional design, comprising a series of cams of suitable design mounted on a common shaft and arranged to close and open electrical contacts according to a prearranged schedule. Automatic operations of the apparatus is achieved thereby.

The pressure readings obtained in the above procedure are slightly higher than the Reid vapor pressure, owing to the compressive effect of introducing the liquid sample into the closed pressure-test vessel, which is initially at atmospheric pressure. The magnitude of this effect can be determined conveniently by feeding a substantially non-volatile liquid into the apparatus. The pressure reading obtained thereby is a true measure of the compression of the gas phase within the pressure-test vessel, and may be subtracted from the readings in subsequent tests to give substantially the true Reid vapor pressure.

While the above example represents the preferred embodiment of my invention, it will be apparent that numerous modifications may be made in accordance with the specification and claim. For example, by adding additional pressure-test vessels and auxiliary valves, pressure tests may be made at an increased rate using the same sampler device. It will be apparent, moreover, that numerous modifications may be made in the mechanical details of my apparatus, in particular the design of the pressure-test bombs and the sampling device, without departing from the spirit of the invention. In particular, the features described herein for saturating the purge gas with water and the means for introducing water into the pressure-test vessels are not essential parts of my invention, but are included optionally to permit the operation of my apparatus in carrying out standard determinations, such as the vapor pressure of gasolines, which arbitrarily require that the sample be water-saturated. In general, it may be said that any modifications or equivalents of my apparatus that would ordinarily occur to those skilled in the art are to be considered as lying within the scope of my invention.

In accordance with the foregoing specification, I claim as my invention:

In an apparatus for measuring the vapor pressure of a flowing liquid stream, a sampling device comprising a cylinder containing a moveable piston, a terminal opening in each end portion of said cylinder on opposite sides of said piston, a supply conduit communicating with said flowing liquid stream and with said terminal openings, a terminal discharge conduit communicating with said terminal openings and with means for measuring vapor pressure, a central discharge conduit communicating with the middle portion of the longitudinal wall of said cylinder whereby said liquid stream is normally continuously discharged after flowing through said cylinder, valves controlling said conduits, means for actuating said valve in said central discharge conduit whereby an accurately measured sample of said flowing liquid stream is isolated within said cylinder, means for actuating said valves in said supply and terminal discharge conduits to alternatively open the inlet and close the outlet at one end of said cylinder and simultaneously close the inlet and open the outlet at the other end thereof whereby said piston is reciprocated by the pressure of the liquid entering said cylinder and whereby said sample is discharged into said means for measuring vapor pressure.

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