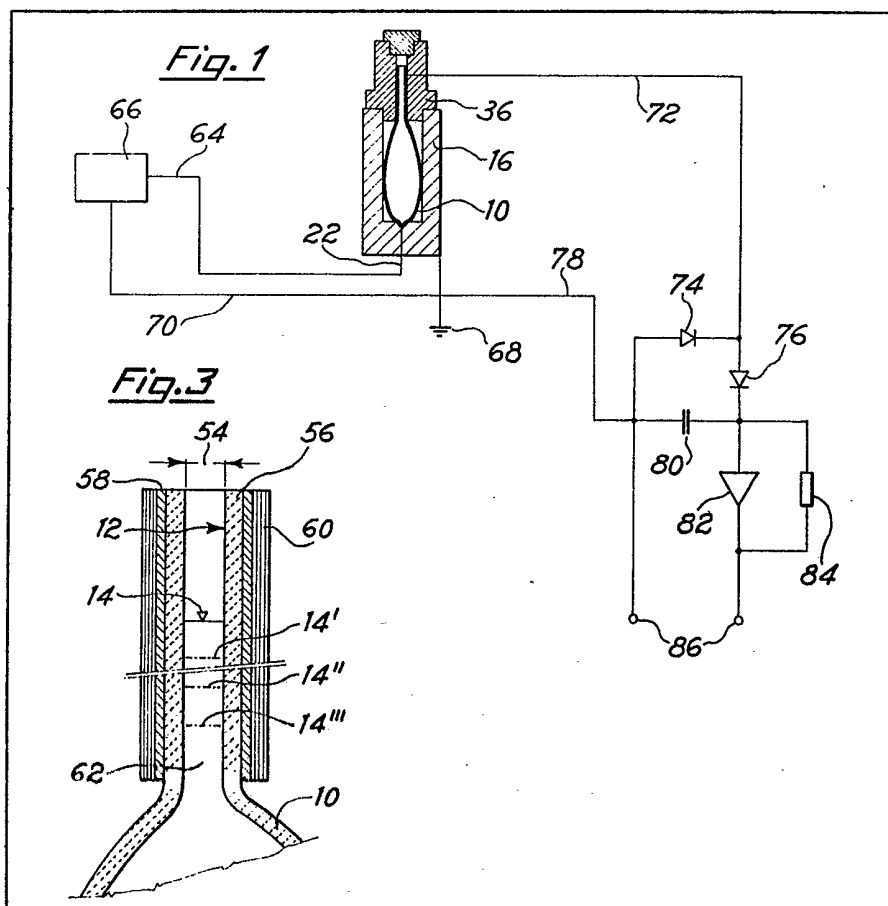(21) Application No **7942853**
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(71) Applicants
**Carlo Erba**
**Strumentazione S.p.A.,**
**Rodano, Milan, Italy**
(72) Inventors
**Giorgio Sisti, Ermete Riva,**
**Pietro Italiano**
(74) Agents
**D. Young & Co.**

(54) **Apparatus for porosimetric measurements**

(57) A porosimeter comprises a glass ampoule 10 having a capillary neck 12 housed in an autoclave 16. A solid sample in the ampoule is immersed in mercury which forms a meniscus 14 in the neck 12. Liquid, preferably transformer oil, is fed via inlet (48) to pressurise the autoclave and cause adsorption of the mercury 62 into the pores of the solid. Mercury adsorption is measured by the position of the mercury meniscus in the neck 12 which is a dielectric 56 of gauged thickness and is surrounded by an electrically conductive armature 58. Adsorption of the mercury is measured by detecting changes in capacity of the condenser formed by the armature 56, the dielectric neck 12 of the ampoule and the mercury 62 due to fluctuations in the position of the meniscus in the capillary. Measuring circuitry includes a square wave generator 66, diode pump circuit 74, 76 and integrator 80, 82, 84.
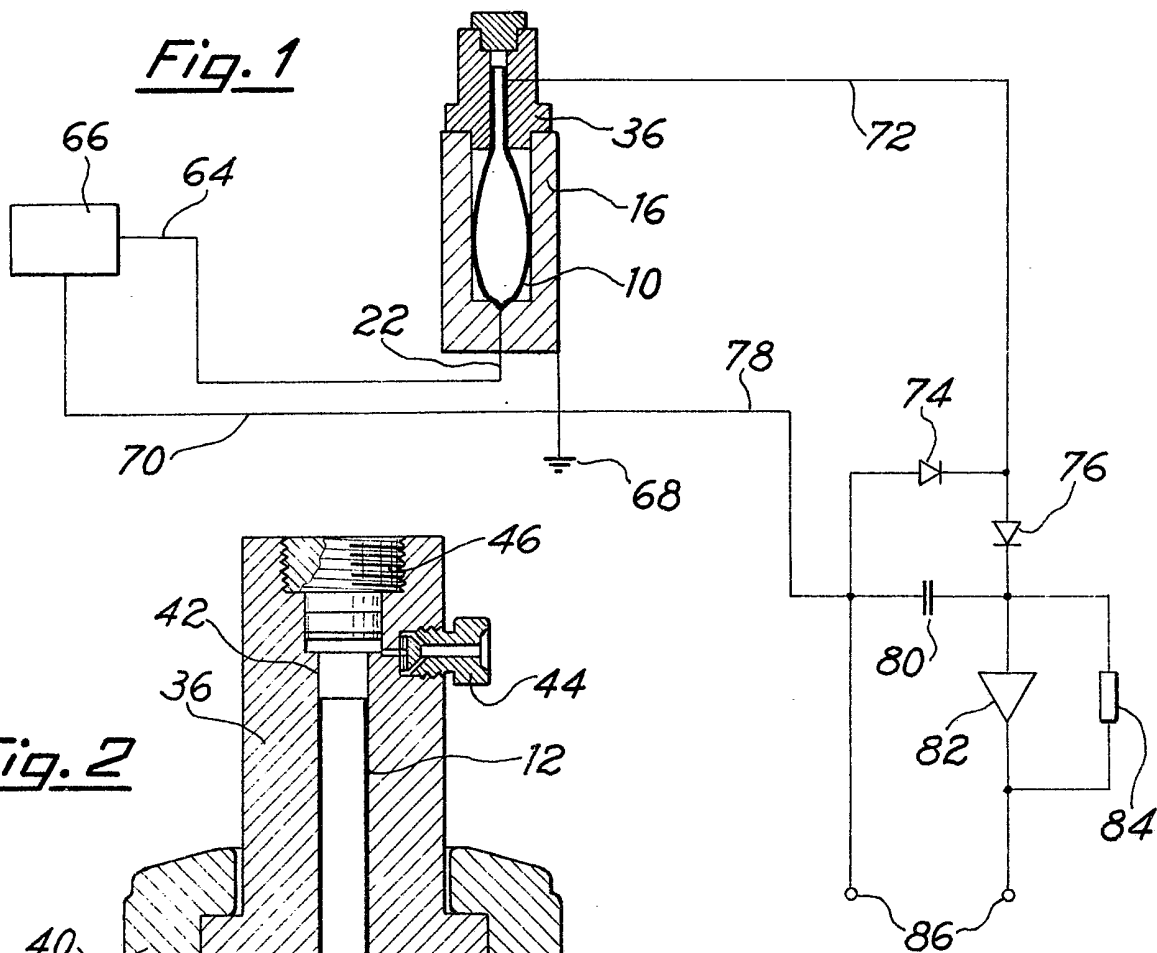


*Fig.1*

*Fig.3*
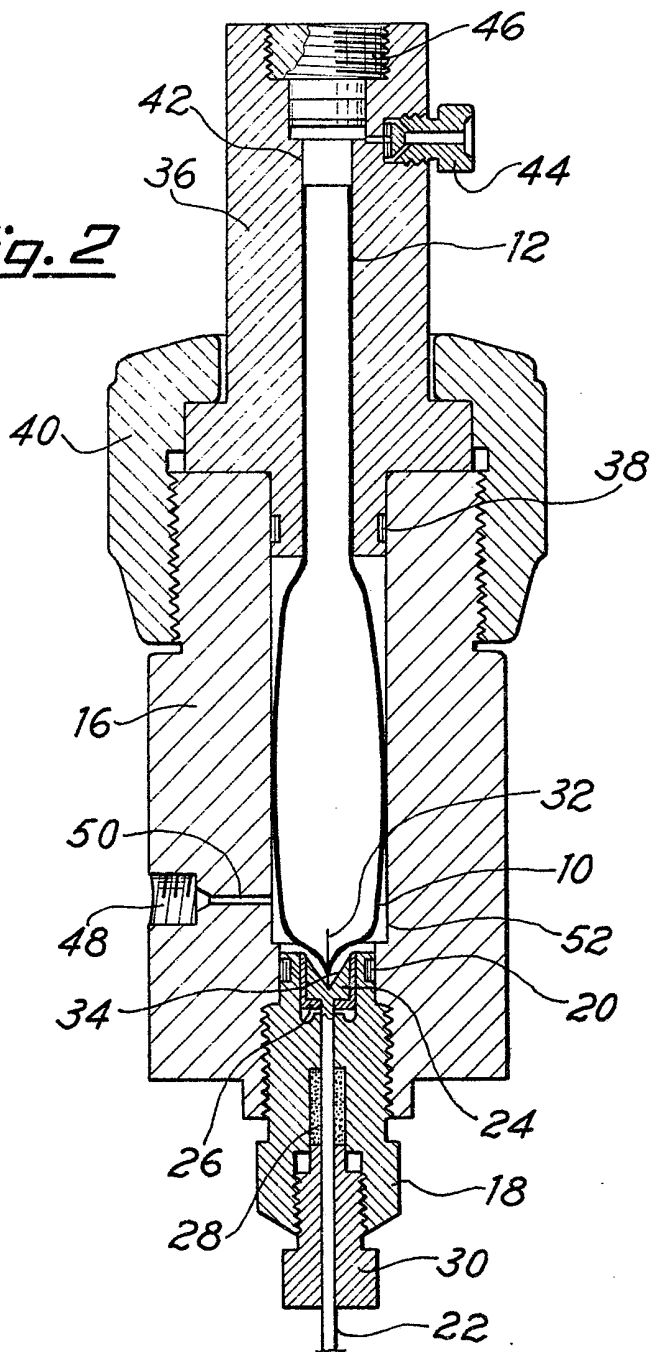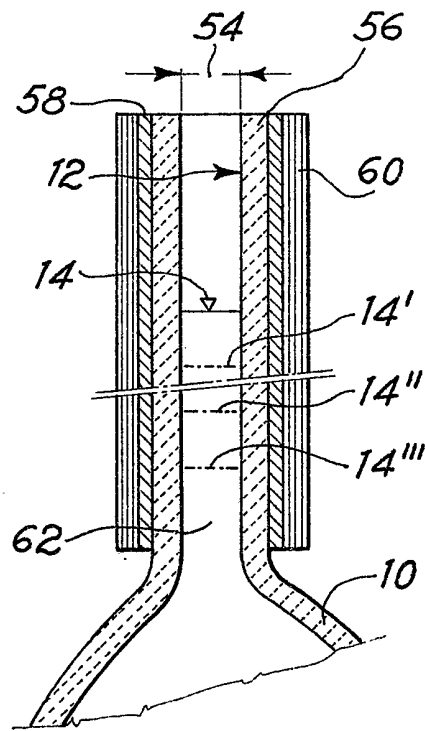
_Fig.1_

66

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36

72

16

10

22

78

70

68

_Fig.2_

46

42

36

44

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18

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30

22

74

76

80

82

84

86

_Fig.3_

54

56

58

12

60

14

14'

14''

14'''

62

10

SPECIFICATION
**Apparatus for porosimetric measurements**

This invention relates to a so-called
porosimeter, that is a measuring apparatus
5  capable of recording volume and size of superficial
microcavities, or pores, in solid substances,
establishing a biunivocal correspondence, at least
per points, between a determined average radius
dimension of pores and their volume. In other
10  words, the apparatus is capable of determining the
volume of the solid pores having a certain average
radius and, subsequently, the volume of the pores
having a lower average radius.

Similar apparatuses are already known and
15  operate according to the so-called Drake method,
which essentially consists in placing the solid
under test into a vessel, creating vacuum in this
vessel, filling same with mercury and submitting
mercury to increasing pressures. For each specific
20  pressure value it is possible to establish an
average radius of the pores into which mercury
penetrates. In other words, each pressure value
corresponds to a value of the pores average
radius, above which pores are filled with mercury,
25  while mercury, on the contrary, does not penetrate
into pores having a lower average radius.

This average radius value is given by the
following relation:

$$Rm = \frac{2\,\sigma \cos\theta}{p}$$

30  where: Rm = average radius of pores, in A;
$\sigma$ = mercury vapour tension at 25°C
(temperature at which analysis is
carried out);
$\theta$ = contact angle between mercury and
35          material under test. This angle is
known for any material and has a
value of approx. 140°, anyway
always ranging between 130° and
150°;
40      p = pressure exerted.

It is therefore obvious that, knowing $\sigma$ and $\theta$
values and measuring p value, it is easy and
automatic to correlate p to Rm and obtain the
latter value from easy knowledge of p, exactly
45  measurable by means of any suitable known
system.

In order to obtain the required biunivocal
correlation between the pores volume and the
relevant average radius Rm, it is then necessary to
50  perform, for each Rm value, that is for each p
value, an exact measurement of mercury volume
variations in the vessel. In fact, as mercury is an
incompressible liquid, each decrease in Hg volume
which can be recorded outside, of course involves
55  the introduction of an equivalent Hg volume into
the pores of the solid under test. The tendency is
to obtain a continuous curve (today achievable
only by extrapolation of points), correlating the
values of volume and average radius of pores. In

60  the practical application of this method, the above
mentioned vessel comprises an ampoule, for
instance a glass one, which is housed in an
autoclave where a suitable liquid is introduced,
partly also penetrating into the ampoule mouth.
65  Once the autoclave is closed, said liquid is put
under pressure with increasing values, to which
negative variations in the ampoule mercury
volume correspond, measured in correlation with
the different pressure values.

70  The main problem faced up to now in the
application of the described Drake method is in
the measurement of the above mentioned
mercury volume variations in the ampoule. In the
known apparatuses of this kind, it has been
75  attempted to solve the problem by using a
capillary of strictly constant diameter in
correspondence with the ampoule neck and
measuring the level variations of mercury in this
capillary. In the known apparatuses, the latter
80  measurement is carried out by connecting the
ampoule bottom, by means of a metal proble
crossing it, to an electric source, using a dielectric
liquid for filling the autoclave and closing the
electrical circuit by means of the mercury in the
85  ampoule and a contact needle penetrating into the
capillary down to the mercury level. The contact
needle is mounted on a support which is rotatable
in a threaded seat so that each turn of the support
corresponds to one lead of the needle to which a
90  certain mercury volume variation corresponds,
measurable on the basis of the capillary diameter.

The analysis is carried out in subsequent steps,
making the needle advance as far as the mercury
level and closure of the electrical circuit, then
95  stopping the needle and increasing pressure until
the circuit opens due to mercury meniscus
lowering, interrupting pressure increase and
making the needle advance again to repeat the
cycle until pressure maximum values are reached.

100  From the above, it is already possible to see
which are the main disadvantages of the known
apparatuses working in the manner described.
First of all, measuring precision is strictly related
to the precision achieved in the needle progress,
105  and the instrument construction is very complex
and expensive, involving numerous drawbacks in
use, especially due to the need of obtaining
perfect sealing in correspondence to a movable
component, such as the contact needle, capable of
110  resisting to the very high pressures involved,
which may reach values of 2000—2500
atmospheres. Secondly, considering that the
volume variations in question are nonetheless
minimum, measurement accuracy is far from
115  being satisfactory. Furthermore, this accuracy is
negatively affected by the possibility that mercury
in the ampoule undergoes superficial oxidation,
which modifies meniscus form in such a way that,
when the latter is taken away from the needle, the
120  contact is not interrupted, this completely altering
measurement result.

Finally, measuring is carried out, as described,
in a non-continuous system, allowing to obtain
only a series of points which must then be

extrapolated to obtain a Volume-Average Radius curve, which complicates and further delays the analysis which already requires a long time to perform due to the described sequence of steps.

5      That being stated, this invention now proposes a new porosimeter, always working according to the above mentioned Drake method and on the basis of the measurement of mercury level variations in the capillary forming the vessel neck,

10   in which the drawbacks of the known apparatuses are avoided and, in particular, the measurement of said level variations is performed without any movable component. Therefore, the above mentioned constructive drawbacks are

15   immediately eliminated and moreover, as will be better shown later on, measuring can be carried out with great rapidity, in continuous cycle, with much higher accuracy without any danger that mercury surface oxidation affects the result, and

20   moreover with ready adaptability to digital display.
       According to the invention, these and other advantages are obtained by means of an apparatus for porosimetric measurements of the type comprising a vessel housing the solid to be

25   analysed immersed into mercury, adapted to be submitted to controlled pressure increases, said vessel including means for electrically connecting mercury with outside and being provided with a mouth consisting of a gauged-diameter capillary,

30   wherein the mercury meniscus is present at any pressure condition during measurement, characterized in that at least said capillary is constituted by dielectric material, has walls with gauged thickness and is externally surrounded by

35   an armature of electrically conductive material, which is connected, at the outside of the zone submitted to pressure and jointly with said mercury electric connection means, in a circuit including a power source and an instrument

40   measuring capacity variations of the mercury condenser constituted, in the capillary, by mercury, the armature and the dielectric part of the capillary itself.
       As a matter of fact, it has been noticed that this

45   mercury condenser and the recording of the capacity variations of same allow to obtain, besides the solution of the above mentioned constructive problems thanks to the elimination of movable components crossing the interface

50   between high pressure zone and atmospheric pressure zone, an accuracy in measuring mercury volume variations 50 to 400 times higher than in the known apparatuses and not affected by possible oxidation of mercury meniscus.

55      Moreover, measuring may be carried out with considerable rapidity and above all in continuity, giving the possibility of directly obtaining continuous curves Average radius-Pore volume and consequently characteristic curves or porosity

60   spectra of the different substances.
       When, according to the already known technique, the vessel is constituted by a glass ampoule placed in an autoclave filled with suitable liquid, it is particularly important that said liquid

65   has a constant dielectric behaviour at any pressure

and, in this respect, it has been noticed that the use of common dielectric oil for transformers has proved to be particularly suitable.
       The invention will be further described with

70   reference to the accompanying drawings, in which
       Fig. 1 is a scheme of the apparatus for porosimetric measurements according to this invention.
       Fig. 2 is an axial section of the autoclave and

75   the ampoule housed in it, for carrying out porosimetric measurements.
       Fig. 3 is a partial section, in magnified scale, of the neck or mouth of the measuring ampoule.
       With reference to the drawing and following

80   the already mentioned Drake method, the cited porosimetric measurements are carried out by placing the specimen to be analysed into a vessel, consisting for instance of an ampoule 10 made of glass or other suitable material, in which vacuum

85   is created; then mercury is introduced up to a preset level in correspondence to the relevant substantially capillary-shaped mouth 12. Said level is indicated in fig. 3 by 14.
       Still according to the known technique, the

90   ampoule 10 is placed into an autoclave better shown in fig. 2 and essentially constituted by a body 16 sealed by a lower fitting 18, with gaskets 20, which is airtightly crossed by an electrode 22 electrically connected to a cone-shaped seat 24

95   supported by the lower fitting 18 and electrically insulated, as shown in 26, from the same. As illustrated, the electrode 22 axially crosses the lower fitting 18 and the sealing in correspondence to the same is ensured by a packing gland 28 and

100  a screwed union 30. The bottom of ampoule 10 is crossed by a conductor 32 connecting the mercury contained in the ampoule with the electrode 22 through a mercury drop 34 placed in the cone-shaped seat of element 24. As it is

105  shown, the ampoule 10 is inserted into the autoclave body 16, which is closed on its upper part by means of a head 36 provided with sealing 38 and removably blocked in position by means of a screwable nut 40. In correspondence to the

110  upper end of its axial opening 42, the head 36 is provided with a device 44 for air ventilation, which can be manually screwed or unscrewed to allow air out through the same or respectively to seal the autoclave internal volume.

115      The opening 42 of the autoclave head 36 fits on the mouth or neck of the ampoule 10.
       Contrary to the known apparatuses, the head 36 of the autoclave can be closed in its upper part, in construction or by means of a suitable closing

120  system, this avoiding problems caused by the need of maintaining sealing through having a movable component such as the contact needle of the known equipments.
       In the shown embodiment 46 indicates a

125  threaded seat to insert a sealing element allowing to bring outside the electrical connection necessary to determine mercury volume variations in the ampoule 10, as it will be better described later on.

130      This sealing element, which can be inserted

into seat 46, may be of the same type as the one
provided at the autoclave bottom and previously
described, or of any other known type suitable to
support high pressures involved, considering that
5   the electrical connection must be insulated with
respect to body 16 and had 36 of the autoclave,
but in no case movable parts are taken into
consideration.
        The illustrated autoclave has in its body 16 a
10   fitting 48, connected through a connector 50 to
the internal cavity 52 of same and externally
connectable to a device (not illustrated) to supply
the cavity 52 of the autoclave with liquid under
pressure. In carrying out porosimetric
15   measurements according to Drake method, once
the ampoule 10 is introduced into the autoclave
and the latter is closed, a suitable liquid is fed into
it, fills the whole autoclave cavity around the
ampoule 10 and penetrates into the mouth 12 of
20   the latter as far as the level of the mercury
meniscus 14 is reached. During this introduction
of liquid, the air present in the autoclave is
completely discharged through vent 44, which is
then closed. After this preliminary operation, the
25   measuring stage is immediately started by
increasing the pressure of the liquid introduced
through fitting 48 and simultaneously recording
mercury volume variations in the ampoule 10 by
measuring the lower of meniscus 14 at different
30   levels 14', 14", 14"', in correspondence to
increasing pressure values. By correlating the
pressure values and the different decreasing levels
of the mercury meniscus 14, it is possible to
obtain, using suitable transformation formulae, a
35   series of values representing the average radius of
pores and the corresponding volume of same, as
previously stated.
        To carry out the above mentioned
measurements, according to the invention, an
40   ampoule 10 is used, the mouth 12 of which,
besides having an exactly gauged internal
diameter 54, presents a wall 56 in a dielectric
material. of exactly gauged thickness, surrounded
by a metal armature 58 in such a way that
45   between the ampoule-contained mercury 62, the
dielectric 56 and the metal armature 58, a
mercury condenser is formed, the capacity of
which obviously varies according to the position of
the meniscus 14 in the capillary 12. The outside of
50   the metal armature 58 is provided with a layer 60
in antifriction material, preferably
polytetrafluoroethylene, for better positioning the
ampoule in the opening of the opening of the
autoclave head 36.
55       In order that said measure of volume or of
mercury level 14 in the ampoule 10 is accurate
and reliable, it is clear that, besides the gauging
conditions of the capillary diameter 54 and the
wall 56 thickness of same, other conditions be
60   necessarily checked, and more particularly it is
necessary that the material forming wall 56 and
ampoule 10, preferably constituted by glass, have
good stability at the operating temperature and
pressure; moreover, it is necessary that the liquid

65   filling the autoclave and penetrating the ampoule
mouth until reaching said meniscus at the
pressure employed, usually from atmospheric
pressure up to 2000—2500 atmospheres. In this
respect, it has been surprisingly noticed that a
70   particularly suitable liquid is constituted by
dielectric oil for transformers, of the commercially
available type.
        To measure capacity variations of the above
mentioned condenser 60, 56, 58, the invention
75   presents a circuit of the type schematically
illustrated in fig. 1. According to this figure, the
electrode 22 is connected, through a conductor
64, to a power source 66 consisting in a square-
wave oscillator, the other outlet of which is
80   grounded in 68 through a conductor 70, together
with the autoclave body 16. The mercury
condenser armature 58 is connected, through a
conductor 72, to a couple of diodes 74, 76 on its
turn connected through a conductor 78 to the
85   oscillator 66, so that said mercury condenser and
the diodes 74, 76 form a so-called diode pump,
constituting a well-known circuital component
commonly used for frequency-tension conversion.
In this particular use, the frequency of the square-
90   wave oscillator 66 is constant, while the
condenser capacity varies according to the level
variations of the meniscus 14. An integration
condenser 80 makes continuous the current
which is supplied to a negative feedback (84)
95   amplifier 82, so that at the terminals 86 it is
possible to obtain a voltage which is directly
proportional to the capacity of the previously cited
mercury condenser. The use of a diode pump for
this measurement is not critical, but particularly
100  advantageous as it allows to solve in a cheap and
functional way the problem of "ward" that is the
elimination of eddy capacities which might affect
the measurement value.
        After what has been stated, the advantages of
105  the new porosimeter according to the invention
are obvious but will be restated. First of all, the
presence of movable contact elements to measure
the mercury level in the ampoule capillary 12 is
avoided. Secondly, detection may be carried out in
110  continuous cycle with the possibility of
immediately tracing average radius-pore volume
curves and with a much higher speed than the one
allowed by the known equipments.
        Moreover, the measure accuracy is not affected
115  by the possible oxidation of mercury meniscus and
is much higher than that of the known
apparatuses. In fact, it is possible to succeed in
recording current variations up to tenths of
microampere, while a 1/10 mm variation in height
120  of the meniscus 14 may correspond to 17
microamperes. Therefore, it is calculated that an
accuracy 50 to 400 times greater than that of the
apparatuses known up to now may be obtained.
Finally, the data obtained at terminals 86 as an
125  analogue voltage signal varying from 0 to 10 volt,
may be easily converted, by means of an
analogue/digital converter, into a suitable digital
form.

CLAIMS

1. A porosimeter comprising a vessel shaped to receive the solid sample to be analysed immersed therein in mercury, said vessel having a neck
5  providing a capillary in which is located, in use, the meniscus of the mercury in which said solid sample is immersed, means for applying pressure to said vessel to cause said mercury to impregnate the pores of said solid, and means for detecting
10  movements of said mercury meniscus in said capillary upon application of pressure to said vessel, wherein at least the neck of said vessel which provides said capillary is constructed of a dielectric material and has walls of a gauged
15  thickness, said neck further being surrounded by an armature of electrically conductive material, thereby to form with said dielectric material and the mercury, when present in the capillary, a mercury condenser, and wherein said detecting
20  means comprise an electrical circuit comprising a power source, said mercury condenser and means for measuring variations in the capacity of said mercury condenser due to fluctuations in the position of said meniscus in the capillary.
25   2. A porosimeter according to claim 1, wherein said vessel is a glass ampoule having an integral neck which provides said capillary and said dielectric wall of gauged thickness.

3. A porosimeter according to claim 2, wherein

30  said ampoule is mounted in an autoclave provided with means for feeding to the autoclave a liquid under pressure, which liquid partly penetrates the neck of the ampoule in contact with the mercury meniscus.
35   4. A porosimeter according to claim 2, when charged with said liquid and wherein said liquid is a dielectric transformer oil.

5. A porosimeter according to any one of the preceding claims, wherein said armature is
40  externally covered by a layer of antifriction material.

6. A porosimeter according to any one of the preceding claims, wherein said electrical power source is a square-wave oscillator and wherein
45  said mercury condenser is connected in a circuit fed by said square-wave oscillator together with at least two diodes which jointly form a diode pump operating at fixed frequency and variable capacity.

7. A porosimeter according to claim 6, wherein
50  said diode pump feeds, through an integration condenser, a negative feedback amplifier, at the terminals of which a difference of potential proportional to the mercury condenser capacity is recorded.
55   8. A porosimeter according to claim 1, substantially as hereinbefore described with reference to the accompanying drawings.