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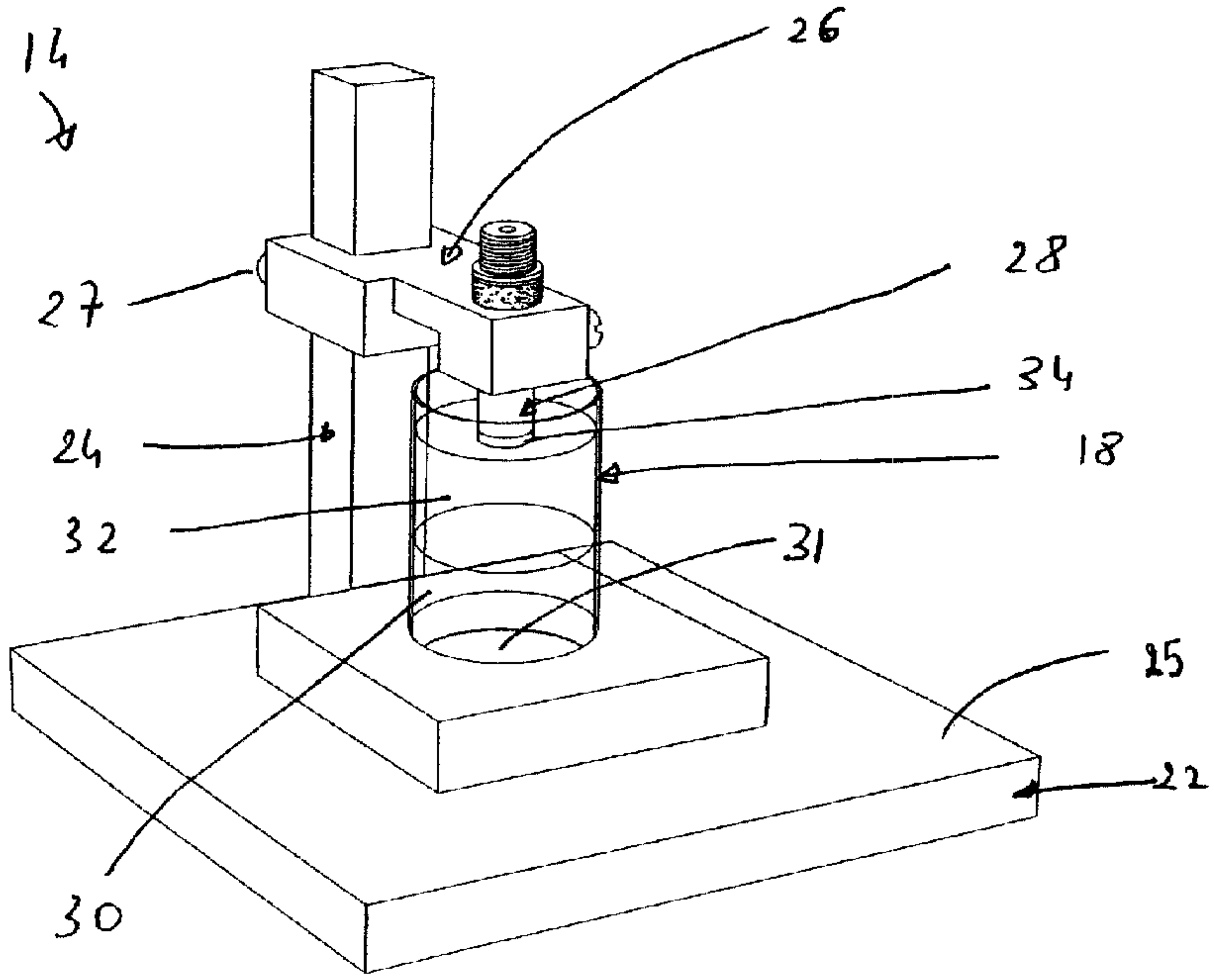
(54) Titre : DISPOSITIF DE MESURE DU COMPORTEMENT DE RETRAIT ET DE LA VARIATION DE MODULE DURANT LA SOLIDIFICATION D'UNE RESINE POLYMERE, ET METHODE CONNEXE

(54) Title: SYSTEM FOR MEASURING SHRINKAGE BEHAVIOUR AND MODULUS CHANGE DURING SOLIDIFICATION OF A POLYMERIC RESIN, AND METHOD THEREFOR



(57) Abrégé/Abstract:

A method and system for measuring the shrinkage behavior and modulus change during the solidification of a polymeric resin is provided, which uses ultrasonic waves propagating through a sample and a medium that acts as a coupling medium. In particular, ultrasonic signals are sent to a surface of a sample. The time of travel of the part of the signal that is reflected at the interface between the sample and the coupling medium back to a sensor, gives the position of the interface between a sample and the coupling medium. This information is used to determine the shrinkage of a sample. The time of travel of the part of the signal that propagates through the thickness of the sample and then reflects from the bottom of the sample at the interface between the sample and the container in which it is contained is used to determine the degree of stiffness of the sample. The time of travel is of the order of one microsecond and the change of thickness of the sample is of tree order of a few hundred micrometers.

ABSTRACT OF THE DISCLOSURE

A method and system for measuring the shrinkage behavior and modulus change during the solidification of a polymeric resin is provided, which uses ultrasonic waves propagating through a sample and a medium that acts as a coupling medium. In particular, ultrasonic signals are sent to a surface of a sample. The time of travel of the part of the signal that is reflected at the interface between the sample and the coupling medium back to a sensor, gives the position of the interface between a sample and the coupling medium. This information is used to determine the shrinkage of a sample. The time of travel of the part of the signal that propagates through the thickness of the sample and then reflects from the bottom of the sample at the interface between the sample and the container in which it is contained is used to determine the degree of stiffness of the sample. The time of travel is of the order of one microsecond and the change of thickness of the sample is of the order of a few hundred micrometers.

TITLE OF THE INVENTION

SYSTEM FOR MEASURING SHRINKAGE BEHAVIOUR AND MODULUS CHANGE DURING SOLIDIFICATION OF A POLYMERIC RESIN, AND METHOD THEREFOR

FIELD OF THE INVENTION

[0001] The present invention relates to polymeric resins and their composites. More specifically, the present invention is concerned with a method and system for measuring the shrinkage behavior and modulus change during the solidification of a polymeric resin.

BACKGROUND OF THE INVENTION

[0002] Nowadays, polymer materials constitute a large proportion of the materials used in engineering applications. Due to their very nature, polymers, particularly thermoset polymers such as epoxies and polyesters, are transformed from a liquid state to a solid state during a curing process. This curing process results in a reduction in volume of a sample, referred to as shrinkage, as well as in a change in stiffness as measured in terms of a modulus.

[0003] Such parameters as shrinkage and modulus need to be monitored in a variety of applications involving polymer resins such as thermoset polymers and polymer composites for example, since they are related to potential problems.

[0004] A first kind of problem can occur with polymer composites used in making components for aircraft structures, automobile parts, pipes or reservoirs for instance, since the shrinkage and change of modulus give rise to dimensional variations and residual stress in the finished product. Models aiming at simulating the behavior of shrinkage and modulus are still inaccurate due the lack of an effective method for measuring experimental data related thereto.

[0005] In the specific case when polymer composites are used for making automotive bodies, the lack of data concerning shrinkage and modulus change have been hindering, for more than 20 years now, the progress of models permitting the computation of adequate conditions in order to obtain a controlled surface finish.

[0006] A further example deals with polymer composites used for making teeth. The resin making up an artificial tooth to be fixed on a crown cools and shrinks onto the shaft of the tooth. A detailed understanding of the shrinkage steps of the resin throughout its solidification history is needed, since in the case where the resin does not shrink properly, the adhesion to the shaft of the artificial tooth is jeopardized, which results in an insecurely mounted tooth. Even though numerous studies are dedicated to develop finite element models of the solidification behavior of the resin, the models are still not accurate enough, due, once again, to the lack of material data.

[0007] As is suggested from the foregoing, adhesives are used for bonding components together in a variety of industrial and everyday applications and the dimensional control of the final parts depends on the shrinkage behavior and change of modulus of the resins upon solidification.

[0008] Therefore, there is a need for an easy and simple method and system enabling measurement of such important properties as the shrinkage and the stiffness of polymeric resins as they are being polymerized.

OBJECTS OF THE INVENTION

[0009] An object of the present invention is therefore to provide an improved method and system for measuring the shrinkage behavior and modulus change during solidification of a polymeric resin.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] In the appended drawings:

[0011] Figure 1 is a simplified block diagram of the system according to an embodiment of the present invention; and

[0012] Figure 2 is a is a simplified perspective view of an apparatus used in the system of Figure 1;

[0013] Figure 3 is a side elevational view of the apparatus of Figure 2;

[0014] Figure 4 is a flow chart of the method making use of the system of Figure 1;

[0015] Figure 5 is a graph of amplitude versus time of a simulated signal as obtained in step 130 of the method of Figure 4; and

[0016] Figure 6 is a second graph of amplitude versus time of a simulated signal as obtained in step 190 of the method of Figure 4.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0017] Generally stated, the present invention provides a method and system, which enable the measurement of the development of shrinkage and the change in stiffness of polymeric resins as they solidify, in an easy and safe way.

[0018] More precisely, the present invention uses ultrasonic waves propagating through a sample and a medium that acts as a coupling medium. Ultrasonic signals are sent to a surface of a sample. A part of the signal (part 1) is reflected (at the interface between a sample and a coupling medium) back to a sensor. Another part of the signal (part 2) propagates through the thickness of the sample and then reflects from the bottom of the sample (at the interface between the sample and the container in which it is contained). The time of travel of part 1 of the signal gives the position of the interface between a sample and the coupling medium. This information is used to determine the shrinkage of a sample. The time of travel of part 2 of the signal is used to determine the degree of stiffness of a sample. The time of travel is typically of the order of one microsecond and the change in the thickness of the sample is typically of the order of a few hundred micrometers.

[0019] Turning now to Figure 1 of the appended drawing, a system 10 according to an embodiment of the present invention will be described.

[0020] The system 10 comprises three subsystems: a first subsystem 12 produces and receives ultrasonic signals; a second subsystem 14 is used to hold a sample; and a third subsystem 16 is used to acquire and analyse signals, and compute test results.

[0021] The subsystem 16 comprises a PC with hardware and software for data acquisition, data treatment, and display of results.

[0022] The subsystem 12 comprises a ultrasonic transducer 28 (UT) (see Figure 2) that can be partially immersed in a coupling medium without damage. The power and time envelope of the ultrasonic signal produced by the subsystem 12 permits, at least, the first two reflections from the interface between the coupling medium and the sample as well as the first reflection from the interface between the sample and the container, to be resolved in amplitude (above signal noise) and in time (between interface reflections). The repetition rate of the ultrasonic transmitter is variable.

[0023] A set-up of the subsystem 14 is shown schematically in Figures 2 and 3.

[0024] The subsystem 14 comprises a container 18 placed on a seat 20, mounted on a base 22. The container 18 is made of material whose dimensional change due to temperature variation is well characterised. The axis of the container 18 is perpendicular to a surface 25 and its location with respect to the surface 25 is fixed.

[0025] A vertical arm 24 is fastened to the base 22 and supports a movable horizontal beam 26. The height of the horizontal beam 26 on the vertical arm 24 can be adjusted, and then fixed by means of a retainer plate 27. The horizontal beam 26 is so designed as to support the UT 28, which is part of subsystem 12, on top of the container 18. The position of the UT 28 can be changed only vertically, as required to accommodate a range of container heights. During use, the elevation of the UT 28 is fixed and the axis of the UT 28 is perpendicular to an inside bottom surface 31 of the container 18.

[0026] The subsystem 14 allows the container 18 to be removed for filling and emptying and put back into the same position relative to the fixed position of the UT 28.

[0027] A sample 30 and a coupling medium 32 are placed in the container 18, the sample 30 being at the bottom thereof and the coupling medium 32 being on top of the sample 30. The mass of the sample 30 is measured for use in subsequent computations. The amount of coupling medium 32 is such as to immerse a transducing element 34 of the UT 28.

[0028] The coupling medium 32 allows the transmission of ultrasonic waves from the ultrasonic transducer 28 into the sample 30.

[0029] It is to be noted that the description hereinabove is only one possible realisation of the apparatus.

[0030] As shown in Figure 1, the system 10 of the present embodiment further comprises the subsystem 16 connected to the subsystem 12. After the ultrasonic signals from the subsystem 12 have interacted with the sample 30 in the subsystem 14, they are acquired in the subsystem 16 as will now be described.

[0031] The acquisition is done using an A/D converter with a sampling frequency at least ten times greater than the central frequency of the UT 28. The subsystem 16 permits the display and storage of signals. It also permits a variable number of signals to be averaged and displayed in practically real time, and the storage of the averaged signal for analysis.

[0032] The analysis according to the method of the present invention comprises determining the various times of flight (TOFs) to the material interfaces. This data along with the process times, t_i, and temperatures, T_i, are used to compute and plot shrinkage and modulus as solidification progresses.

[0033] The method 100 according to an embodiment of the present invention will be best understood with reference to the flow chart of Figure 4.

[0034] In a first step 110, the vertical position of the UT 28 is set and fixed so that the container 18 can be easily placed in its assigned position and so that the UT 28 is adequately immersed in the coupling medium 32 during testing.

[0035] Then, in step 120, a first coupling medium 32 is selected. Any coupling medium in which the speed of sound at a current test temperature is well characterised can be used, since this step mainly aims at determining the distance "L" between the UT 28 and the interface between the coupling medium 32 and the container 18. Conveniently, distilled water may be used as the coupling medium for that stage. This coupling medium 32 is added to the container 18 until the UT 28 is partially immersed.

[0036] The transmission of ultrasound into the contents of the container 18 can then be started. The measure of the TOF between the first and second echoes from the interface between the coupling medium 32 and the container 18 is recorded as TOF_L. The value of the distance "L" between the UT 28 and the interface between the coupling medium 32 and the container

18 is computed using the definition of speed as being the ratio of the distance over time, knowing the speed "v(T)" of sound in the coupling medium 32 at a temperature "T", according to the following equation:

$$L = v\,(T)\ X\ (TOF_L\ /\ 2)\quad (1)$$

TOF_L corresponds to twice the distance, L (step 130).

[0037] Keeping the UT 28 in its fixed position, the container 18 is removed, and the coupling medium 32 is thoroughly removed therefrom (step 140).

[0038] In a following step 150, the container 18 is weighed, before the sample 30 is carefully introduced into the weighed container 18. Then, the container 18 containing the sample 30 is weighed again so as to calculate the mass m of the sample 30.

[0039] A second coupling medium 32 is then selected. This time, the coupling medium must not only be one in which the speed of sound is well characterised versus temperature, but also one that is compatible with the sample 30 and the test conditions. In particular, the coupling medium 32 is inert with respect to the sample 30, is less dense than the sample 30 and does not mix with the sample 30. Moreover, the speed of sound in the selected coupling medium 32 must be well characterised over the temperature range of the solidification process (step 160).

[0040] The container 18 is seated back in place, with the sample 30 inside (step 170), before the coupling medium 32 is carefully added to the container 18 on top of the sample 30 so that the sample surface is not disturbed by the flow, and so as to partially immerse the UT 28 (step 180).

[0041] In step 190, ultrasound transmission is activated into the content of the container 18, producing signals comprising first and second echoes from the interface between the coupling medium and the sample, and the first echo from the interface between the sample and the container. These signals are stored together with the corresponding process time t_1, coupling medium temperature T_{c1}, and sample temperature T_{s1} , where the subscript "1" indicates test record number 1.

[0042] The initial data record where n = 1, is then analysed as described further hereinbelow (step 200).

[0043] If the solidification process is not completed, the process is started over from step 190 and the data record number is incremented by 1. Otherwise the test is terminated.

[0044] It is to be understood that in step 160, the second coupling medium is different from the first coupling medium used in step 120 in case this first coupling medium is distilled water. However, it is possible to use a similar coupling medium at both steps 120 and 160, provided this coupling medium meets the requirements cited in step 160.

[0045] During the analysis step 200 above-mentioned, measurements of times of flight (TOF) between reflections from the different interfaces are made, and these times are converted to lengths. The lengths are used to compute the following test parameters: the thickness h (t), the shrinkage s (t), the volume V (t), the density ρ(t), and the modulus M (t), of the sample. As the sample solidifies, measurements of TOF_i and temperature T_i are made at times t_i. These measurements are used to compute the values of the parameters as functions of process time t_i. The analysis step 200 of the method according to an embodiment of the present invention will now be detailed.

[0046] The analysis first comprises computing the thickness of the sample 30, referred to as h_1 (t), by measuring the TOF between the first and second echoes from the interface between the coupling medium 32 and the sample 30, referred to as $TOF_{c1.}$ As can be best seen in Figure 2, the thickness h_1 of the sample 30 is given by the relation :

$$h_1 = L - w_1 \quad (2)$$

where L is the fixed distance between the UT 28 and the inside bottom surface 31 of the container 18 as computed hereinabove through equation (1), and w_1 is given by the following relation:

$$2w_1 = v_{c1} (T_{c1}) \times TOF_{c1} \quad (3)$$

where $v_{c1} (T_{c1})$ is the speed of sound in the coupling medium 32 at temperature T_{c1}. Then the value h_1 is computed by substituting L from (1) and w_1 from (3) in (2).

[0047] Secondly, the analysis involves computing the volume V_1 of the sample 30. Considering that the volume of the sample 30 is the product of thickness thereof by the cross sectional area A_1 of the container 18, the following relation is used :

$$V_1 = h_1 \times A_1 \quad (4)$$

where the cross sectional area A_1 of the container 18 is given by:

$$A_1 = \pi \times D_1^2 / 4 \quad (5)$$

and $D_1 = C_1/\pi$ (6), wherein D and C are the diameter and circumference, respectively, of the container 18, giving:

$$A_1 = \pi \times [C_1/\pi]^2 / 4 \quad (7)$$

Substituting (7) into (4) gives the following equation:

$$V_1 = h_1 \times \pi \times [C_1/\pi]^2 / 4 \quad (8)$$

[0048] In general, because the cross sectional area of the container 18 may change because of the coefficient of thermal expansion (CTE) of the container material, the circumference C varies as follows:

$$C_n = C_1 \times [1 + \alpha(T_{sn} - T_{s1})] \quad (9)$$

where α is the CTE of the container 18 and the subscript n indicates the number of the data record. Substituting (9) into (8), the result for the general case reads as follows:

$$V_n = h_n \times \pi \times \{\{\{C_1 [1 + \alpha(T_{sn} - T_{s1})]\}/\pi\}^2 / 4\} \quad (10)$$

[0049] Therefore, for the first data record, i. e when $n = 1$, equation (8) holds. It is to be noted that the circumference C of the container 18 is to be calculated from the diameter of the container 18 measured at the initial test temperature when $n = 1$. The CTE of the material of the container 18 may be known from published data or from measurements on the container.

[0050] A third computation performed during the analysis relates to the shrinkage s_1 of the sample 30. Shrinkage is generally defined as a percentage using the following equation:

$$s_n = [(V_1 - V_n) / V_1] \times 100 \quad (11)$$

where the subscript n indicates the number of the data record. For the first data record $n = 1$ and $s_1 = 0$.

[0051] A further parameter determined during the analysis step is the density ρ_1 of the sample, defined by: $\rho_1 = m / V_1$ (12).

[0052] Additionally, the analysis comprises the computation of the speed of sound in the sample 30, labelled v_{s1} (T_{s1}). The definition of speed implies v_{s1} $(T_{s1}) = 2^*h_1 / TOF_{s1}$ (13), where TOF_{s1} is the time of flight between the first echo from the interface between the coupling medium 32 and the sample 30, and the first echo from the interface between the sample 30 and the container 18, and corresponds to twice the distance travelled by the sound wave in the sample 30.

[0053] Finally, the analysis permits the determination of the modulus of the sample 30, noted M_1, and defined by the following equation :

$$M_1 = \rho_1 X [v_{s1} (T_{s1})]^2 \quad (14)$$

where the terms on the right hand side are taken from equations (12) and (13) cited hereinabove.

[0054] As will be obvious from the foregoing, the temperature of the sub-system 14 is monitored. Moreover, a temperature control system can be incorporated to permit studies using various solidification cycles.

[0055] It is to be noted that the UT 28 acts in the pulse/echo mode, i.e., it is both the transmitter of the ultrasound and the receiver of ultrasound that is reflected from material interfaces.

[0056] The method of the present invention may be used to select a suitable coupling agent and to identify suitable couples polymer/coupling medium.

[0057] An example of the above-described method will now be described, by means of results from a numerical simulation, as a way of example only, in relation to Figures 5 and 6.

[0058] After the UT is set in position as required in step 110, distilled water may be chosen as a first coupling medium, in step 120, and the UT 28 is activated (see step 130). Figure 5 shows a first and a second echo (300 and 310 respectively) from the interface between the coupling medium 32 and the container 18. The TOF_L, as measured from the time difference between the two echoes, amounts to 97.09 X 10 $^{-6}$ seconds. The speed of sound in distilled water at T = 21.45° C can be assessed by means of a relation known in the art (e.g., Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, Group II: Atomic and Molecular Physics, Vol. 5 – Molecular Acoustics, Hellwege, K.-H. and Hellwege, A.M., eds., Springer-Verlag, Berlin, 1967, p.69), which gives v (T) = 1487 m/s. The distance between the UT 28 and the interface between the water and the container 18 is given by means of the relation (1) cited hereinabove (step 130). It is found, in the present example, to have a value of 0.07219 m.

[0059] As required in step 140, the container 18 is then removed from the seat 20 and emptied of the coupling medium, which is herein distilled water, while taking care of keeping the fixed position of the UT 28. The sample is weighed: here, it weights m = 0.0782 kg. Low-density oil for example may be selected as a second coupling medium (step 160), since the relation giving the speed of sound in the oil as a function of temperature is known. In this case, the relation is: v_c (T) = -5.2495 X T + 1502.9. Then the container 18 with the sample inside is positioned again in place (step 170), and the low-density oil is added on top of the sample in sufficient quantity to partially irnmerse the UT 28 (step 180).

[0060] For this example, a general data record, referred to as x, is considered and it is assumed that the data for record 1, at t = 0, are the following: T_{c1} = T_{s1} = 22.1° C, C_1 = 0.15708 m, V_1 = 71.755 X 10^{-6} m^3. The signal for record x is stored, and the following values are recorded: t_x = 270 minutes, T_{cx} = 23. 4° C. and T_{sx} = 28.6° C (step 190). A simulated signal is shown in Figure 6, with a peak 320 corresponding to a first echo from the interface between the coupling medium and the sample; a second peak 330 corresponding to an echo from the interface between the sample and the container; and a third peak 340 related to a second echo from the interface between the sample and the coupling medium.

[0061] The analysis step (200) then begins, related to the general data record where n = x, as follows. The TOF_{cx} from the stored signal is measured. It is, in the present example, $TOF_{cx} = 52.97 \times 10^{-6}$ s. Using the equation (3) given hereinabove, with the known value $v_c (T_{cx}) = 1380$ m/s, a value of 0.03655 m for $w_x = (1380 \text{ m/s} \times 52.97 \times 10^{-6} \text{ s})/2$ is found. Using next the equation (2) cited hereinabove, the sample thickness is computed, yielding $h_x = 0.07219 - 0.03655 = 0.03564$. The volume of the sample is computed by means of the relation (10), knowing the properties of the container 18, as follows :

$$V_x = h_x \times \pi \times \{\{\{C_1 \times [1 + \alpha(T_{sx} - T_{s1})]\}/\pi\}^2 / 4\}$$

with constant $\alpha = 3.25 \times 10^{-6}$ per degree Celsius, $C_1 = 0.15708$ m, and $T_{s1} = 22.1°$ C. The volume of the sample is thus found to be $V_x = 69.975 \times 10^{-6}$ m^3

[0062] The shrinkage is then computed using (11) as follows:

$$s_x (270) = \{[71.755 \times 10^{-6} - 69.975 \times 10^{-6}] / 71.755 \times 10^{-6}\} \times 100 = 2.48\%$$

[0063] The sample density ρ_x amounts to 1117.543 kg/ m^3 ($\rho_x = 0.0782 / 69.975 \times 10^{-6}$), and the speed of sound in the sample, $v_{sx} (T_{sx})$ is calculated as $v_{sx} (T_{sx}) = 2 \times h_x / TOF_{sx} = 913$ m/s where TOF_{sx} is the time of flight between the first echo (320) from the interface between the coupling medium and the sample and the first echo (330) from the interface between the sample and the container, and corresponds to twice the distance travelled in the sample ($TOF_{sx} = 78.09 \times 10^{-6}$ s). Finally, the sample modulus M_x is calculated using (14): $M_x = 1117.543 \times 913^2 = 0.931$GPa. When the solidification process is not completed the above steps should be repeated from step 190 on by incrementing the data record number by 1. Otherwise, the test is terminated.

[0064] As will be apparent to people in the art, the method of the present invention enables the measurement of the history of shrinkage and stiffness at the same time, for both liquid and solid, and for different temperatures.

[0065] The present invention provides a valuable knowledge as far as the control of the dimensions and of the stiffness of final product are concerned, in the field of high tech applications such as aircraft, space components, dental applications, automobiles etc., or in applications of new polymeric resins, in which developers need to learn how these new resins perform in terms of shrinkage and stiffness.

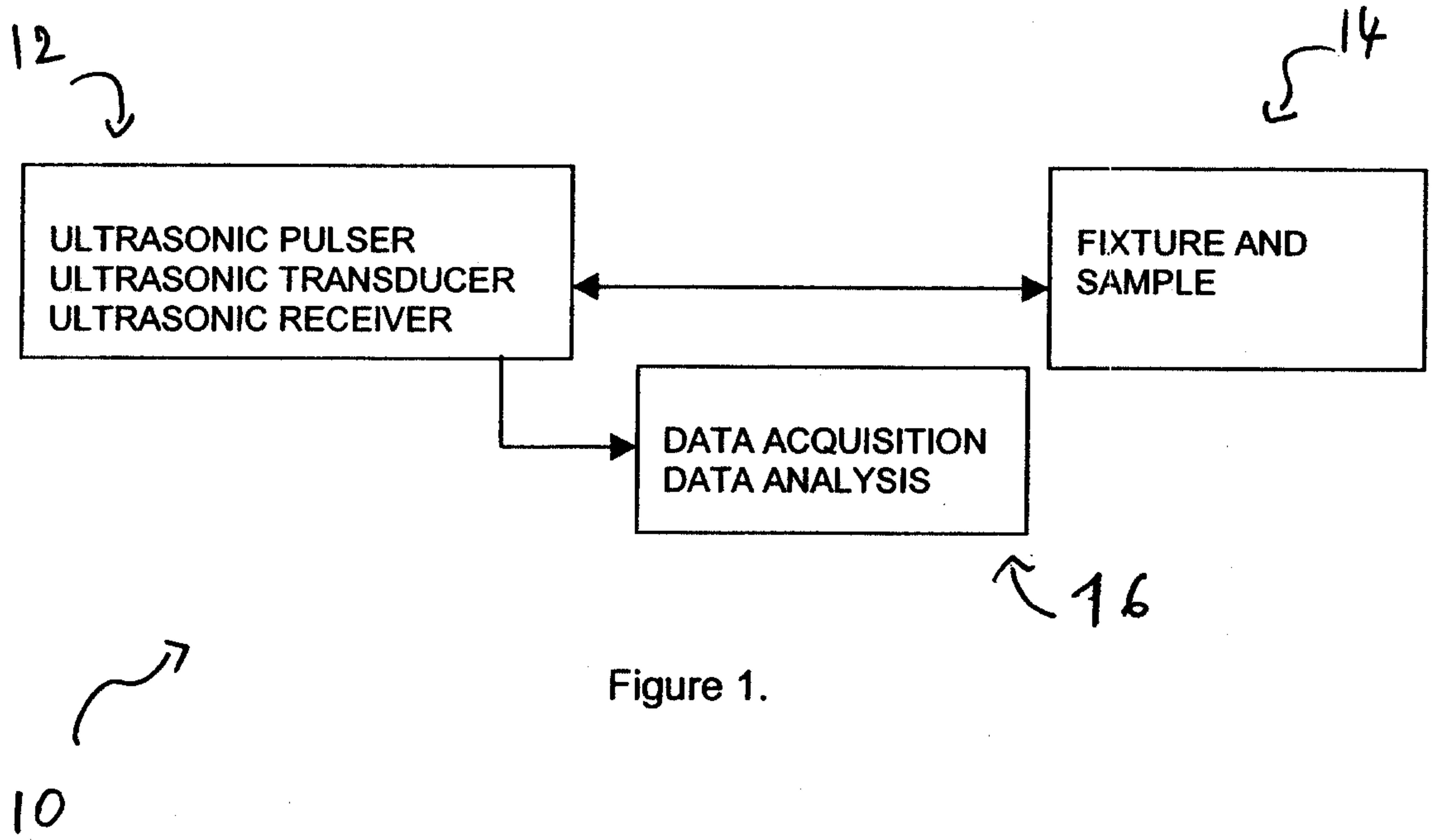
[0066] Furthermore, it is to be noted that the method of the present invention is simple. It does not require exotic materials that may pose environmental hazards. It does not require high pressure and it takes little time to set up and to operate.

[0067] Although the present invention has been described hereinabove by way of preferred embodiments thereof, it can be modified, without departing from the spirit and nature of the subject invention as defined in the appended claims.

WHAT IS CLAIMED IS:

1. A method for measuring the shrinkage behavior and modulus change during solidification of a polymeric resin making use of ultrasonic as generally described herein.

2. A system for measuring the shrinkage behavior and modulus change during solidification of a polymeric resin making use of ultrasonic as generally described herein.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14
ULTRASONIC PULSER
ULTRASONIC TRANSDUCER
ULTRASONIC RECEIVER
FIXTURE AND
SAMPLE
DATA ACQUISITION
DATA ANALYSIS
16
10

Figure 1.

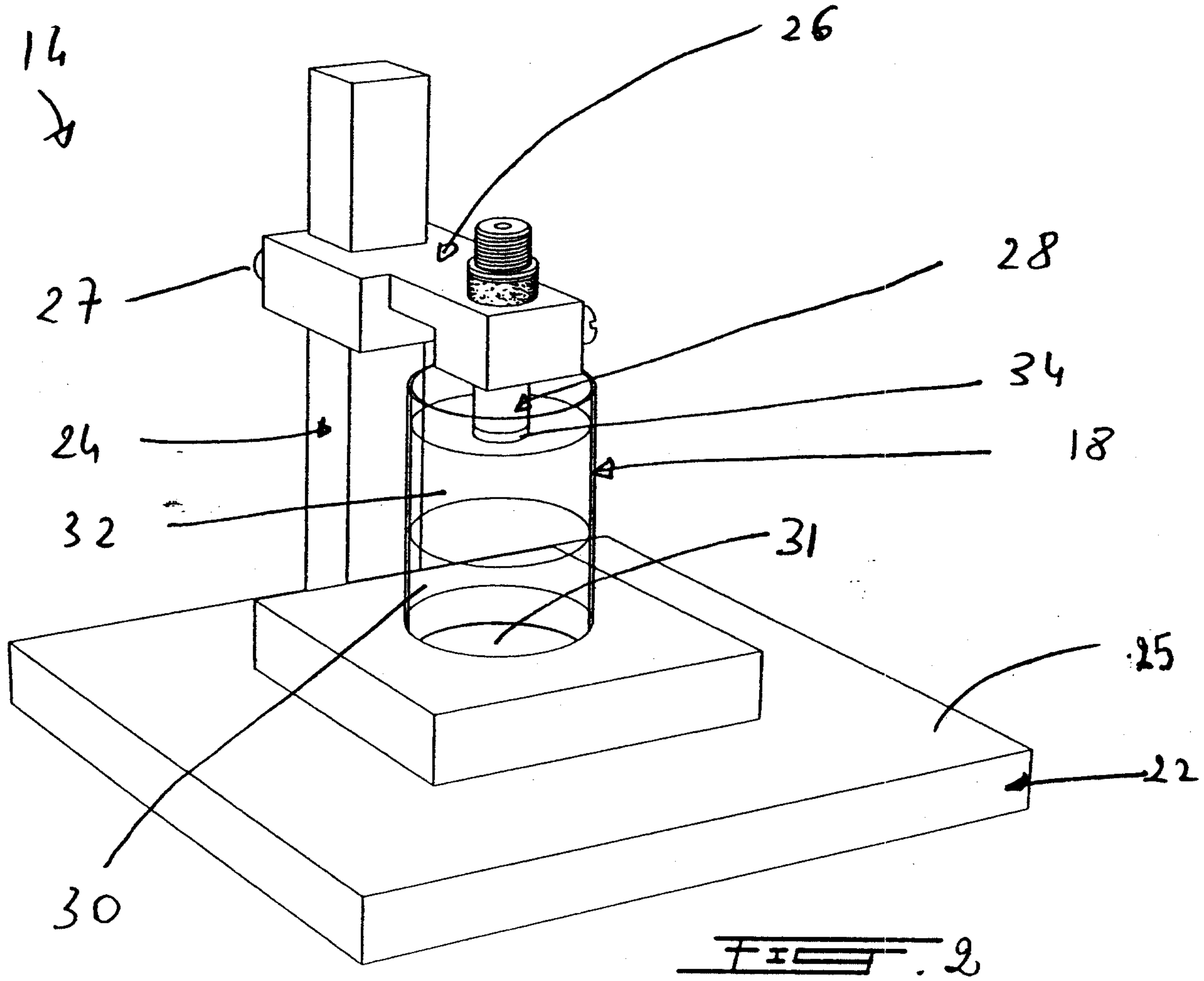
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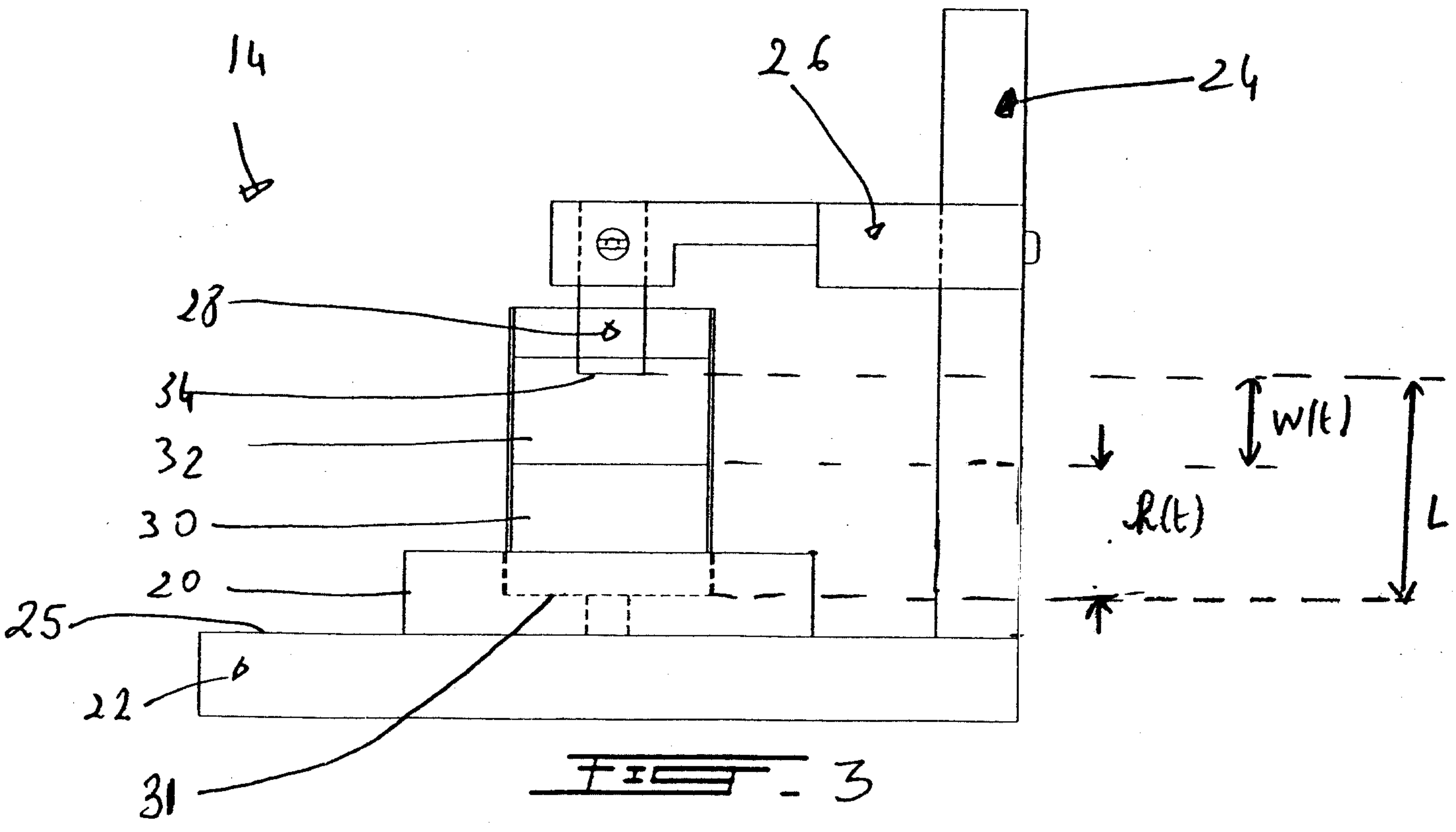
FIG. 2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W(t)
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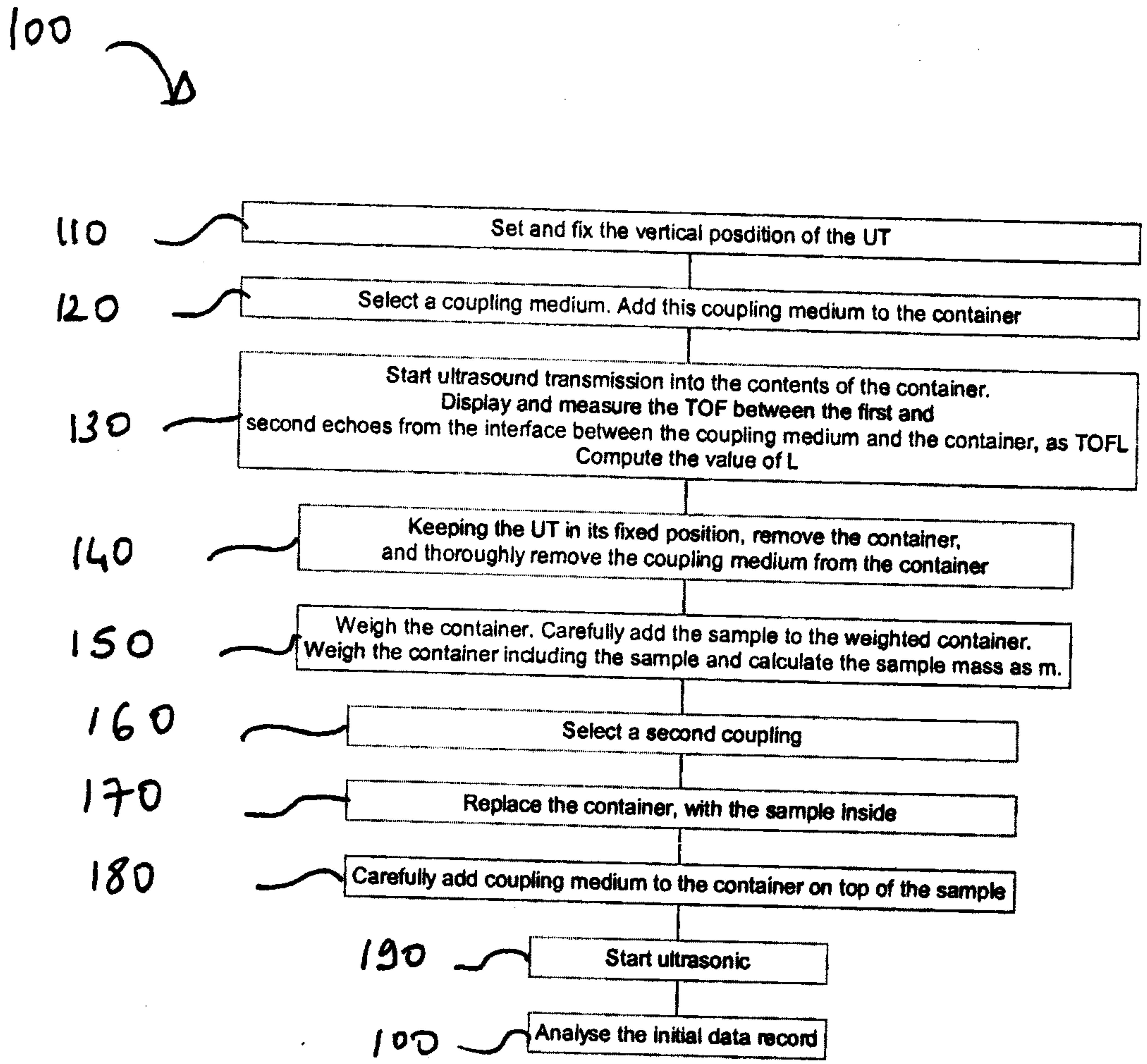
FIG. 3

Figure 4


100
110
Set and fix the vertical posdition of the UT
120
Select a coupling medium. Add this coupling medium to the container
130
Start ultrasound transmission into the contents of the container.
Display and measure the TOF between the first and
second echoes from the interface between the coupling medium and the container, as TOFL
Compute the value of L
140
Keeping the UT in its fixed position, remove the container,
and thoroughly remove the coupling medium from the container
150
Weigh the container. Carefully add the sample to the weighted container.
Weigh the container including the sample and calculate the sample mass as m.
160
Select a second coupling
170
Replace the container, with the sample inside
180
Carefully add coupling medium to the container on top of the sample
190
Start ultrasonic
100
Analyse the initial data record

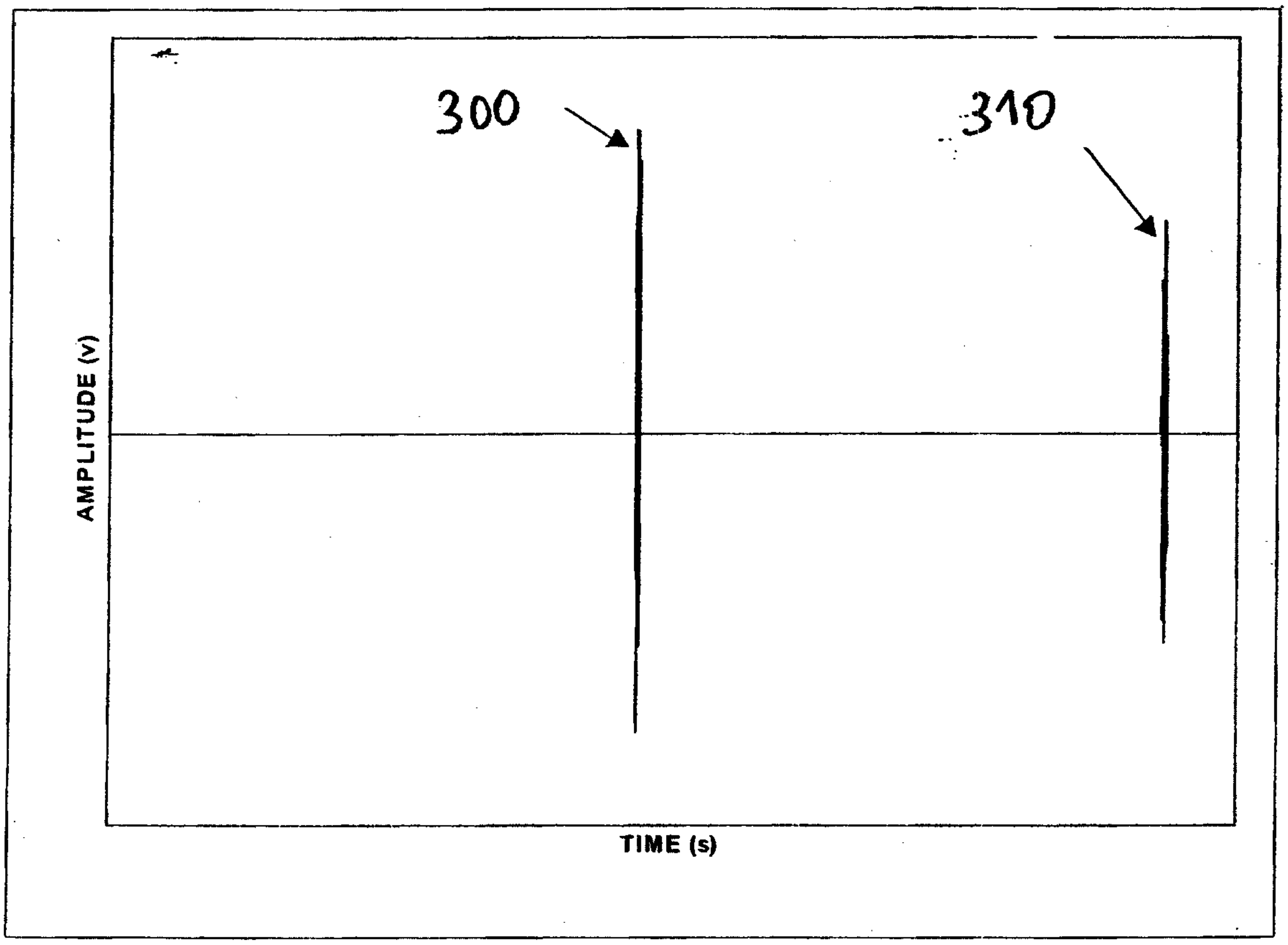


Fig. 5

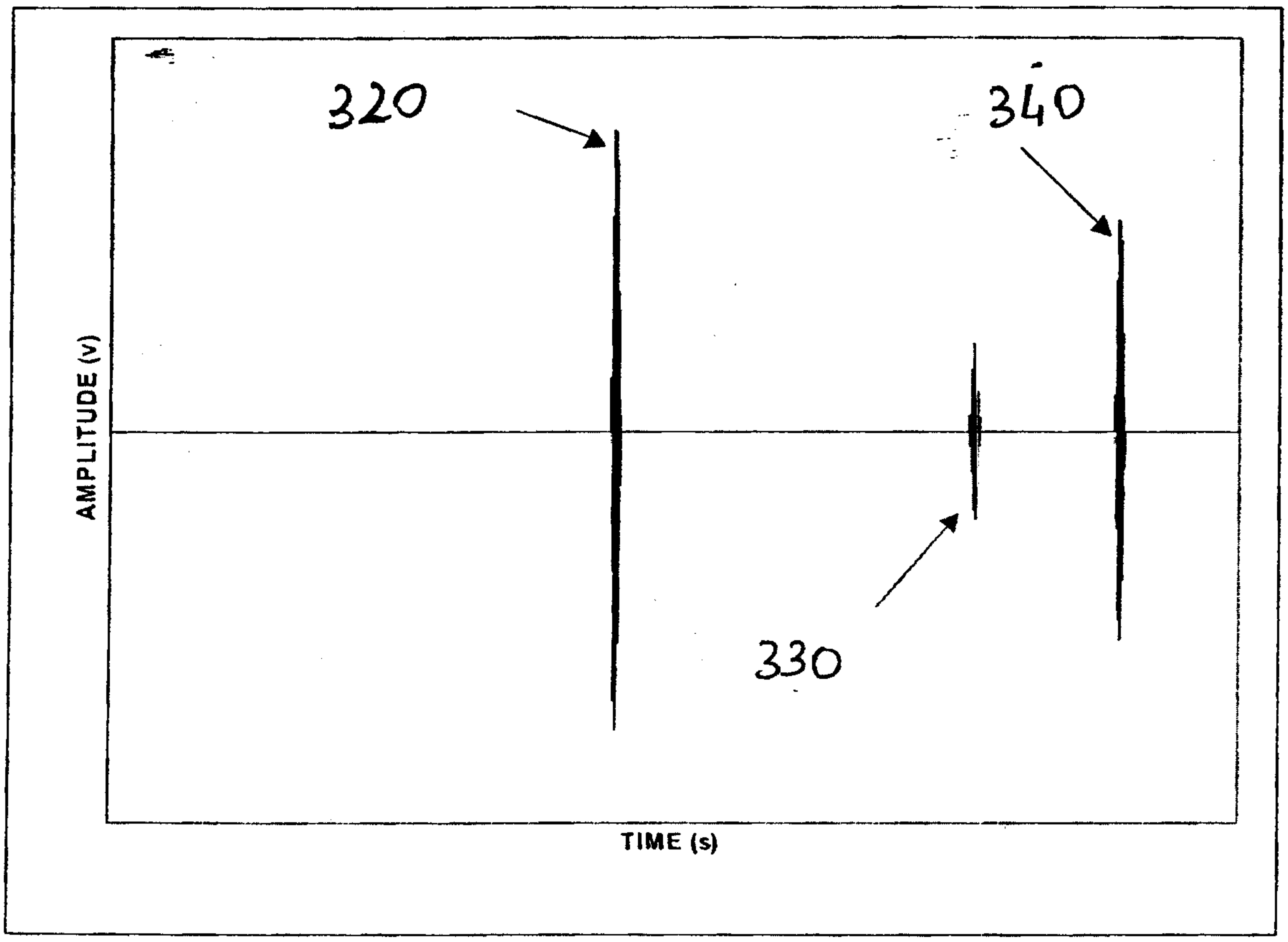
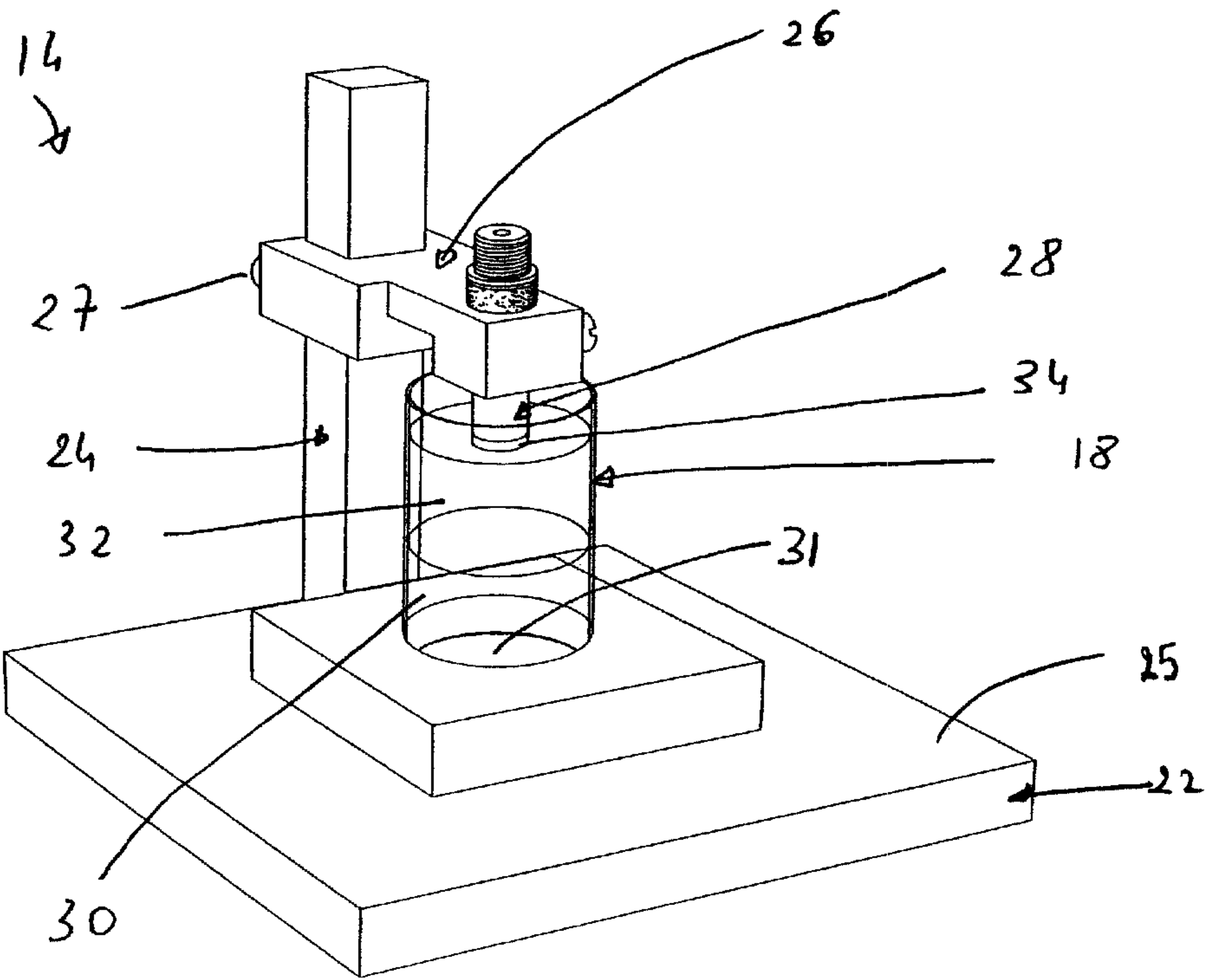


Fig.6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