



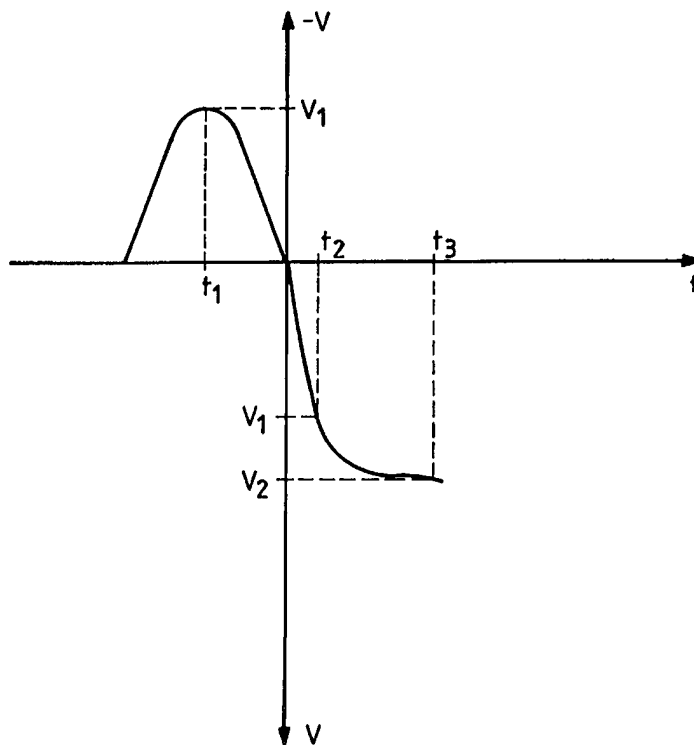
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(21) International Application Number: PCT/FI98/00142 (22) International Filing Date: 17 February 1998 (17.02.98) (30) Priority Data: 970671 18 February 1997 (18.02.97) FI (71) Applicant (for all designated States except US): AHLSTROM MACHINERY OY [FI/FI]; Sentnerikuja 2, FIN-00440 Helsinki (FI). (72) Inventor; and (75) Inventor/Applicant (for US only): MATULA, Jouni [FI/FI]; Kuusistontie 5, FIN-57600 Savonlinna (FI). (74) Agent: AHLSTROM MACHINERY OY; Patent Dept., P.O. Box 18, FIN-48601 Karhula (FI).		(81) Designated States: BR, CA, DE, JP, KR, SE, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report. In English translation (filed in Finnish).

(54) Title: METHOD OF DETERMINING PULP PROPERTIES

(57) Abstract

The present invention is related to a method of determining the amount of gas in a liquid. The method is particularly well suited for determining the amount of both the gas in the form of bubbles and the gas dissolved in pulp, i.e. in various fiber suspensions of paper and pulp industry. The invention is advantageously applied to the control and regulation applications of removal of air in the short circulation of a paper machine.



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METHOD OF DETERMINING PULP PROPERTIES

The present invention relates to a method for determining the amount of gas contained
5 in liquid. The method according to the invention is particularly well applicable in
determining of the amount of gas, both in the form of bubbles and in dissolved state,
contained in the various fiber suspensions, i.e. pulps, of the pulp and paper industry.
The invention is advantageously applied in control and regulation systems of degassing
in the short circulation of a paper machine.

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The pulp used in the manufacture of paper, which is normally supposed to contain
water, brushed out fibers and required additives, also contains air and other gases
depending on the apparatus, the processes and the grade of pulp.

15 Air entrains into the pulp with high-consistency pulp, circulation waters, pulping and
mixing. Also leaking vacuum seals and open turbulent flows introduce air into the
process. Chemical and microbiological reactions release gases in the pulp, the most
common gas being CO₂. Also other gases may be present such as O₂, SO₂, H₂S, and
Cl₂.

20

Gas exists in the pulp in two basic forms: as bubble-formed air and as dissolved gas.
Bubble-formed air may be divided into free and residual air. Free air means air
bubbles moving freely in the liquid between fibers. Residual air is formed when free
air is dispersed mechanically for example in a grinder. Microbubbles produced in this
25 way adhere firmly to the surface of the fibers or to the lumen. Dissolved gases
constitute various gases dissolved in the liquid, for example CO₂, O₂, N₂, etc. In this
form, gases usually do not cause problems and they do not affect the pulp properties
but, due to changes in the pressure, the temperature or the chemical balance, dissolved
gases may turn into bubbles. The total volume of air varies greatly depending on
30 conditions and the grade of pulp. For example in the head box feed flow, there is
normally 1 - 4 % by volume of air.

- The most visible influence of air in the paper machine is froth and air bubble on the wire generated by free air. Air in the form of bubbles cause fluctuations in the consistency as air bubbles present in the pulp displace by their volume fibers and water.
- 5 Residual air has the most significant influence on the pulp properties and the quality of paper. Fibers which contain much residual air are thickened onto an open surface. While moving the fibers bump and adhere to each other. Residual air impedes the operation of a paper machine and degrades the paper quality.
- 10 Disturbances caused by air may be avoided by carefully designing the apparatus and processes to prevent air from being mixed into the pulp and/or by removing air entrained in the pulp. Air may be removed advantageously by a DECULATOR[®] degassing apparatus by Ahlstrom Machinery Corporation.
- 15 A large number of different apparatus, ways and methods for determining the amount of gas present in liquid both in a dissolved and a gaseous state.

DE-B-23 62 158 relates to measuring the amount of gas dissolved in liquid by means of subatmospheric pressure. According to the method of the publication, the sample

20 vessel consisting of a lower container having a pressure air chamber disposed therein and of a measuring tube disposed in the upper portion of the container is filled with the liquid to be measured and the end of the measuring tube is closed. Subsequently, air is withdrawn from the pressure air chamber so as to create a slight subatmospheric pressure in the measuring tube. Due to the subatmospheric pressure, gas is separated

25 from the liquid and the liquid level in the measuring tube decreases indicating the amount of the separated gas. According to the publication, this measurement must be repeated a few times to find out the true volume of gas dissolved in the liquid.

US-A-4,329,829 relates to measuring the amount of gas bubbles contained in liquid.

30 According to the method described in the publication, a sample of liquid is introduced into a container and it is pressed under two different pressures; between the pressing actions the pressure of the sample is relieved to be atmospheric. The two volume

changes are registered and the amount of gas in bubble form in the liquid is calculated according to Boyle's law .

US-A-4,862,729 relates to an improvement of the method of the above US publication
5 and deals with measuring gas amounts which are small and easily soluble in liquid. According to the method of the publication, a sample of liquid is introduced into a measuring chamber, the volume of the chamber is increased to two different volumes and the corresponding pressures are measured, relieving the pressure of the sample between the measurements to be atmospheric. The amount of gas dissolved in the
10 liquid may be determined based on Boyle's law. The publication states further that separation of the dissolved gas is slow.

US-A-4,700,561 relates to an automatic on-line gas amount measuring apparatus. According to the publication, a sample of liquid is collected to a cylinder, the liquid in
15 the cylinder is subjected to pressure and by determining the change of volume caused by the pressure change, the amount of gas may be calculated based on Boyle's law. The publication concentrates to a large extent on the structures and operations required by the automation of the measuring apparatus.

20 DE-A-43 22 017 deals primarily with determining of the carbon dioxide content of soft drinks. In other words, it relates to determining the amount of gas dissolved in liquid. The publication discloses how the separation speed of the gas dissolved in liquid may be substantially increased for example by means of ultrasound.

25 However, the measuring methods described in all the above publications have one drawback. All the publications deal with determining the amount of either gas dissolved in liquid or gas in bubble form present in the liquid. None of them suggests determining the amount of both dissolved gas and bubble-formed gas during the same measuring operation. Measurement of this kind is, however, essentially important in
30 many fields of industry. For example, in the pulp and paper industry, it is of primary importance to know the volume of gas in the bubble form and the volume of dissolved gas in the liquid as bubble-formed gas may as such cause foaming and other problems.

Further, as far as the pressure of the process remains unchanged or increases, the gas dissolved in the liquid does not cause problems but when the process pressure drops the gas dissolved in the liquid accumulates into bubbles and in favourable conditions creates for example foam.

5

The main object of the present invention is to provide an improved method, when compared with prior art methods, for measuring bubble-formed air and dissolved gases in the pulp.

10 A method according to a preferred embodiment of the invention reaching the above objective comprises the following stages:

a) liquid to be studied is introduced into a measuring container;

b) the liquid in the rest state (V_0 , p_0) is subjected to superatmospheric pressure p_1 whereby its volume decreases by V_1 ;

15 c) the amount of gas in bubble form is determined based on the volume change V_1 caused by the pressure change p_1 ; and is characterized in that

d) the liquid in the measuring container is released to its rest state (V_0 , p_0);

20 e) subatmospheric pressure p_2 is applied to the liquid in the rest state (V_0 , p_0) in the container whereby the subatmospheric pressure p_2 releases at least part of the dissolved gas to bubble form and the volume increases by V_2 ;

f) the amount of gas dissolved in liquid is determined at least by means of the volume changes V_1 and V_2 .

25 The method according to the invention is illustrated in detail in the appended drawing figures of which

Fig. 1 illustrates schematically a preferred embodiment of the invention; and

Fig. 2 illustrates schematically a measuring arrangement for carrying out an

30 embodiment of the method according to the invention.

Figure 1 illustrates a measuring system according to the invention. Probes for measuring at least the temperature T , the pressure p and the dissolved gas, for example oxygen O_2 , have been provided in a measuring container 10. Further, the measuring container has been provided with an ultrasonic detector US and apparatus L for determining the movement of a piston 20 in a cylinder 22 annexed to the measuring container. The measuring container 10 has also valves 12, 14, 16 and 18 for at least supply and discharge of pulp, and supply and discharge of flushing water, respectively. Thus, after the measuring has been completed the measuring container may be drained and flushed. If desired, the whole measuring operation may be automated.

10

The measuring apparatus according to the present invention may be used to measure air and gases either at atmospheric pressure or at the pressure of the process. The measurement at the atmospheric pressure may be arranged to take place automatically for example so that while the pulp to be measured flows in a smooth flow through the measuring container 10, a push on a measuring button closes the feed valve of the apparatus and after a delay also the discharge valve which ensures that the pressure in the measuring container 10 has stabilized. The volume defined by the valves is predetermined precisely and known by the processor of the apparatus so that the influence of the position of the piston 20 on the volume may be determined. At the process pressure, the measurement is performed so that the push on the measuring button closes the discharge valve of the apparatus and after a delay also the feed valve. Then an accurately known volume, at the process pressure, is retained between the valves.

20

The apparatus works in principle so that movement of the piston 20 in the cylinder 22 changes the volume of the measuring container - cylinder combination. Pressing the piston 20 from the rest state, i.e. volume V_0 , pressure p_0 , deeper into the cylinder 22 (i.e. in the figure upwards) the pressure in the measuring container 10 increases and the volume of the entire measuring container - cylinder combination decreases when the gas in bubble form is compressed. A preferred method of performing the measurement is to push the piston into the cylinder until the pressure has reached a desired reading p_1 , for example 50 kPa superatmospheric pressure, after which the measuring device

30

registers the volume change V_1 in the measuring container - cylinder combination based on information given by the piston position probes. With this information the amount of bubble-formed gas in the pulp may be calculated according to Boyle's law. The measuring pressure p_1 used should preferably be fairly low in order to avoid dissolving of the gas from the bubbles to the liquid. According to a preferred embodiment of the invention, measuring of the amount of dissolved gas is started by pulling the piston 20 from the rest position in the cylinder 22 outwards (in the figure downwards) so that the volume of the measuring container increases by V_1 measured from the rest state. Then the pressure in the measuring container - cylinder combination decreases to $-p_1$, for example 50 kPa subatmospheric pressure (corresponding to the superatmospheric pressure used in the measurement of the bubble-formed gas) and the dissolved gas tends to be separated into bubbles. Figure 2 demonstrates most concretely the measurement, depicting the volume change as a function of time. The figure indicates that the volume decreases from the rest state by V_1 when the piston is pressed into the cylinder with a given pressure (for example 50 kPa). Correspondingly, the volume increases from the rest state by V_1 when the pressure is reduced to a corresponding subatmospheric pressure p_1 , (-50 kPa) in the measuring container 10. When the same subatmospheric pressure p_1 is maintained for a longer time in the measuring container the piston 22 moves gradually further outwards (to the reading V_2) which means that dissolved gas has been separated from the pulp in the measuring container 10 into bubbles. By determining the change of volume $V_2 - V_1$ caused by the separation of dissolved gas, the share of the dissolved gas may be determined by means of pressure for example according to Boyle's law (in the general form $p \cdot V/T = \text{constant}$, and when the temperature is constant, $p \cdot V = \text{constant}$).

25

Another way of performing the measurement is to use different pressures. In other words, the superatmospheric pressure used in the determining of the bubble-formed gas may be for example 50 kPa and the subatmospheric pressure used in the determining of the dissolved gas for example -70 kPa. In this case, the determining of the volume of the bubble-formed gas performed at superatmospheric pressure is done by registering the pressure p_1 and the volume change V_1 and the amount M_1 of the bubble-formed gas is determined using these readings and according to Boyle's equation. Subsequently,

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the sample is returned to its initial state, volume V_0 , pressure p_0 , and after that the same sample is subjected to a desired subatmospheric pressure p_2 , whereby the change of volume will be V_2 . These pressure and volume readings are used to further determine by means of Boyle's law the total amount M_2 of the gas separated from the sample
5 whereby M_2 contains both the bubble-formed and the dissolved gas. When the amount of the bubble-formed gas is known to be M_1 , the amount of the dissolved gas may be calculated by subtraction $M_2 - M_1$. As it is usually desirable to express the gas volume as a percentage, this should be calculated separately.

10 As particularly the measuring of dissolved gas may be slow the measuring device may be provided with an ultrasonic vibrator. During the relatively strong cavitation-like vibration caused by the ultrasound the releasing speed of the dissolved gases into bubbles is multiplied and the measuring time is correspondingly shorter. In automatic measuring, the measuring of the dissolved gas is stopped after a predetermined time t
15 and the amount of the released gas is calculated according to Boyle's law .

Subsequently, the piston is returned to its initial position and a new measurement may be started. When the measuring device is used to continuously monitor the process the interim period between the measurements is set as required. Efficient operation of the
20 measuring device prefers as short interim periods as possible. In automatic operation, the measurement is preferably repeated every 5 - 10 minutes.

A measuring device for dissolved oxygen or a corresponding gas may also be connected to the measuring device. The device measures the true amount of the dissolved gas or
25 the amount in percentage.

According to a preferred embodiment of the present invention, measuring probes T and P for momentary measuring of the temperature and the pressure of the pulp have been connected to a device for measuring the bubble-formed and the dissolved gas. Several
30 measuring members measuring the temperature and the pressure and the position of the precision piston required for the determining of the gas amount may be disposed in the

process to be monitored. In this way, the monitoring of the pulp properties becomes remarkably more efficient.

Further, it should be noted that when the amount of dissolved gas is determined in most cases in each point from liquids or fiber suspensions of very similar type the measuring may be accelerated as follows. When the measuring is started, the volume of dissolved gas is determined as accurately as possible in each point for example by using much time for performing each measurement, possibly also by using an ultrasound vibrator. By determining the separation speed of the dissolved gas, i.e. observing as a function of time how fast gas is separated (this may be illustrated graphically for example by a curve drawn in a coordinate system the axes of which are the volume of the separated gas in per cent and the time) is possible to predict the amount of gas in a liquid even on the bases of a very short measuring time. In other words, the observation of the separation speed may give a result according to which 90 % of the total gas volume is separated from a certain liquid in certain conditions in ten minutes and half of the total gas volume is separated in two minutes. Then the further measurements may be performed in two minute periods and the curves may be used to determine the true volume of dissolved gas. When a microprocessor or a computer is used to process the measuring results, the data from the inspection of the separation speed of dissolved gas in a large number of different liquids in different conditions may be input into the computer and thus even changes in conditions do not slow down the measurements in the mill. It is even possible to record into the processor/the computer of the device data on the separation speed of various liquids in various conditions obtained in laboratory conditions in advance before the device is brought to the mill which allows the device to be used at once from the beginning quickly and in a practical way.

As is disclosed by the above examples the invention solves the problem of determining the volume of the gas dissolved in pulp, which has not been solved before. The method of the present invention is able to determine the amount of the dissolved gas with an accuracy which is adequate for most purposes. Further, the measuring of the amount of the dissolved gas may be accelerated by employing an ultrasonic vibrator and thus the degassing of the short circulation may be controlled better and thereby paper of higher

quality may be produced. Also, it should be noted that, in addition to the short circulation of paper manufacture, the invention may be applied in feed pumps, screens, washers etc. of a pulp production process or in general, in the parts of the pulp production process in which measuring of air volumes is necessary. The examples
5 described above do in no way intend to limit the invention from what has been defined in the appended patent claims.

As the above description discloses, a method of measuring gas volumes has been developed which is remarkably more efficient, more accurate and simpler than prior art
10 methods. Further, the method of the invention may be provided to pay attention to temperature variations either by performing temperature calibration mathematically based on the data obtained from the temperature probes or by arranging a constant temperature in the measuring container. It should be noted that the measuring method of the invention has been described above by way of example, only, and the real scope
15 of protection of the invention is defined by the appended patent claims, alone.

We claim:

1. A method of determining the amount of gas, both in the form of bubbles and in dissolved state, the method comprising the following stages:

- 5 a) the liquid to be studied is introduced into the container;
b) the liquid in a rest state (V_0 , p_0) is subjected to superatmospheric pressure p_1 , causing the volume to decrease by V_1 ;
c) the volume of bubble-formed gas is determined based on the volume change V_1 caused by the pressure change p_1 ;
10 **characterized** in that
d) the liquid in the measuring container is released to the rest state (V_0 , p_0);
e) the liquid in the measuring container in the rest state (V_0 , p_0) is subjected to subatmospheric pressure p_2 whereupon the subatmospheric pressure releases at least part of the dissolved gas into bubble form and the volume increases by V_2 ;
15 f) the amount of dissolved gas in the liquid is determined at least by means of the volume changes V_1 and V_2 .

2. A method as recited in claim 1, **characterized** in that in stage e), the pressure $p_2 = -p_1$, and thus the difference of the volume changes $V_2 - V_1$ corresponds to the amount of
20 the released dissolved gas.

3. A method as recited in claim 2, **characterized** in that the volume change $V_2 - V_1$ caused by the release of gas is determined as a function of the time spent and the amount of the released gas is determined based on the volume change $V_2 - V_1$.
25

4. A method as recited in claim 2 or 3, **characterized** in that in stage f) the amount of the released gas is determined based on the volume changes $V_2 - V_1$ mentioned and on the subatmospheric pressure p_1 mentioned.

30 5. A method as recited in claim 1 or 2, **characterized** in that during measurement of the amount of the dissolved gas, the releasing speed of the gas bubbles is monitored instead of the time spent and the measurement is stopped when the speed clearly decelerates.

6. A method as recited in claim 1 or 2, **characterized** in that during measurement of the amount of dissolved gas, the measurement is performed in one or several stages and the last measurement is performed at the maximal subatmospheric pressure of the measurement device.
7. A method as recited in claim 1 or 2, **characterized** in that after the measurement of the amount of gas has been finished, the measuring container is drained and flushed whereupon the piston returns to its initial position.
8. A method as recited in claim 1 or 2, **characterized** in that the measuring container may be provided with a separate inlet flush valve and a separate outlet flush valve.
9. A method as recited in claim 1 or 2, **characterized** in that a measuring device for dissolved oxygen is connectable to the gas determining device.
10. A method as recited in claim 1 or 2, **characterized** in that the gas determining device measures also the momentary temperature and the pressure of the pulp.
11. A method as recited in claim 1 or 2, **characterized** in that the gas determining is performed at the process pressure or at the atmospheric pressure.
12. A method as recited in claim 1 or 2, **characterized** in that the temperature of the measuring container is constant.
13. A method as recited in claim 1, **characterized** in that in stage f) the amount of both the bubble-formed gas and the dissolved gas is determined based on the volume V_2 and the pressure p_2 and the amount of the dissolved gas is further determined by subtracting from this the amount of the bubble-formed gas determined in stage c).

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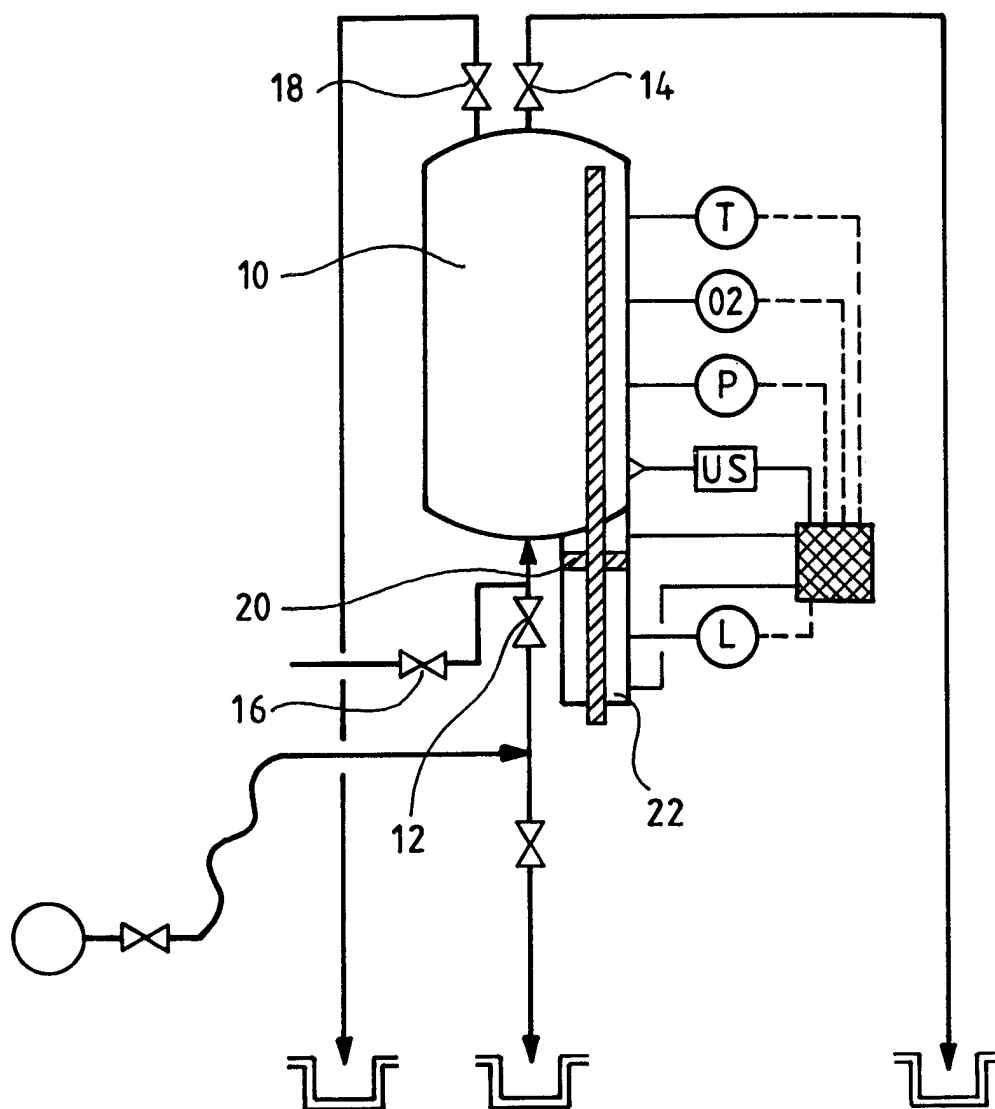


FIG. 1

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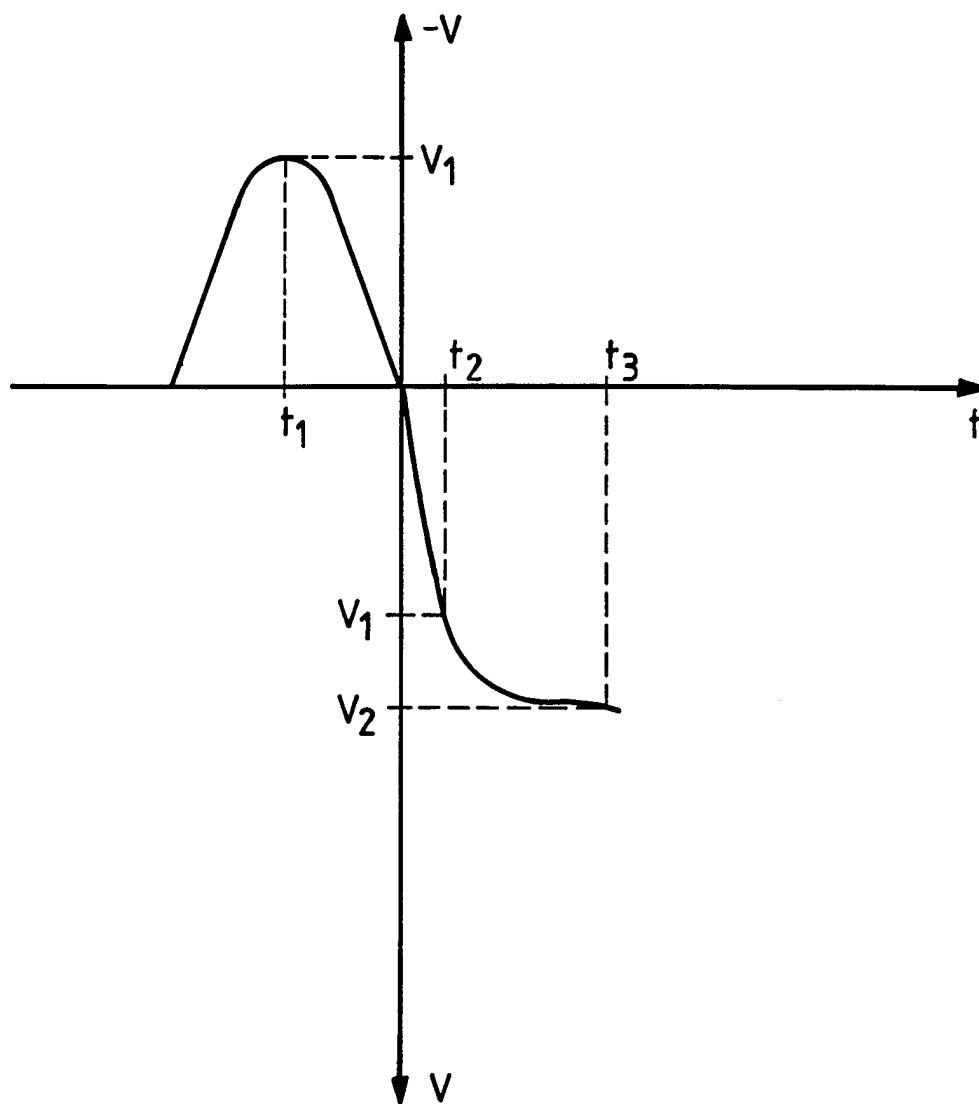


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00142

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G01N 7/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 2362158 B (J.M. VOITH GMBH), 16 January 1975 (16.01.75) --	1-13
A	US 4329869 A (KENICHI TODA), 18 May 1982 (18.05.82) --	1-13
A	US 4700561 A (DOUGHERTY, STEVEN J.), 20 October 1987 (20.10.87) --	1-13
A	US 4862729 A (KENICHI TODA ET AL), 5 Sept 1989 (05.09.89) --	1-13

☒ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

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Date of the actual completion of the international search 11 May 1998	Date of mailing of the international search report 01-06-1998
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Britt-Marie Lundell Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00142**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 4322017 A1 (OTTO TUCHENHAGEN GMBH & CO KG), 12 January 1995 (12.01.95) -- -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/04/98

International application No.

PCT/FI 98/00142

Patent document cited in search report			Publication date	Patent family member(s)	Publication date
DE	2362158	B	16/01/75	NONE	
US	4329869	A	18/05/82	DE 3021255 A,C JP 56021036 A	19/02/81 27/02/81
US	4700561	A	20/10/87	CA 1282256 A EP 0258399 A WO 8705107 A	02/04/91 09/03/88 27/08/87
US	4862729	A	05/09/89	DE 3720904 A JP 1833999 C JP 5032694 B JP 63082342 A	31/03/88 29/03/94 17/05/93 13/04/88
DE	4322017	A1	12/01/95	NONE	