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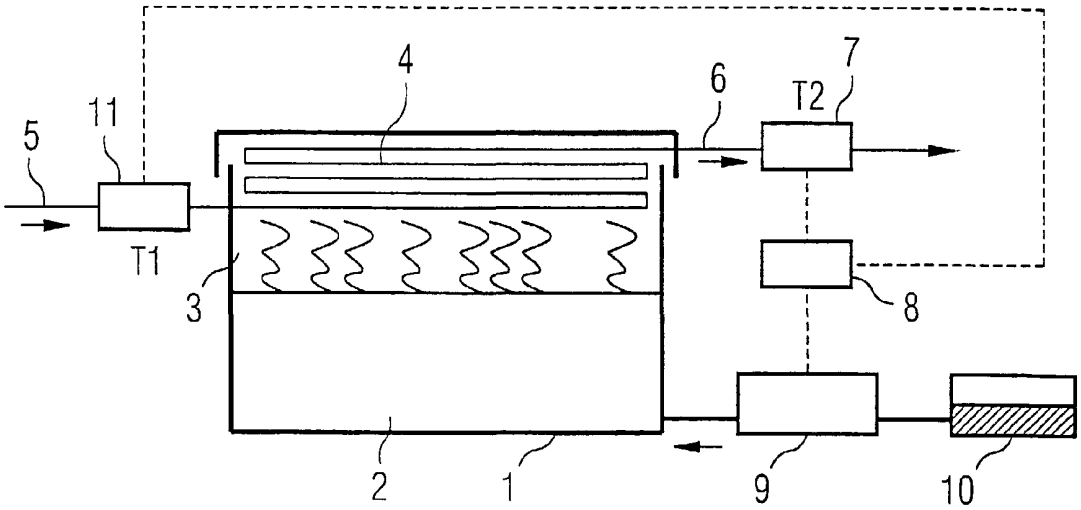
(54) Title: METHOD AND APPARATUS FOR MEASURING AND CONTROLLING THE WATER CONTENT OF A WATER CONTAINING LIQUID MIXTURE



(57) Abstract: An apparatus for measuring the water content of a water containing liquid mixture (2) contained in a tight chemistry tank (1) comprises a heating device for controlling the temperature of said liquid mixture to a temperature near the boiling point of said liquid mixture, a cooling medium system (4), disposed at the top of the tight chemistry tank (1), having a cooling medium inlet (5) and a cooling medium outlet (6), a temperature measurement system (7) for determining the temperature difference between cooling medium inlet (5) and cooling medium outlet (6), and a computing device (8) for calculating the water content of said liquid mixture (2) from said temperature difference. An apparatus for controlling the water content of a water containing liquid mixture (2) comprises the apparatus for measuring the water content of a water containing liquid mixture as defined above, a tank (10) for supplying water to said liquid mixture, and a control system (9) for adjusting the amount of water supplied from said tank (10) on the basis of the water content measured by said apparatus for measuring the water content.

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Method and apparatus for measuring and controlling the water content of a water containing liquid mixture

The present invention generally relates to an apparatus and a method for measuring as well as controlling the water content of water containing liquid mixture contained in a tank.

In particular, the present invention relates to an apparatus and a method for the in-situ control of the water content in so-called HOT PHOS (hot phosphoric acid) baths.

Usually, in the manufacture of semiconductor integrated circuits, HOT PHOS baths are used for wet-etching of silicon nitride. Silicon nitride is generally used as a masking layer. When it becomes necessary to remove the silicon nitride mask, normally, wet etching with hot phosphoric acid at 160°C with approximately 85 wt-% H_3PO_4 is used.

$$Si_3N_4 + 6H_2O \xrightarrow{H_3PO_4} 3SiO_2 + 4NH_3 \qquad \text{(Equation 1)}$$

Since the etching rate of silicon nitride is more than ten times higher than the etching rate of silicon dioxide, silicon nitride is selectively etched. However, two important factors influence the etching rate of both silicon nitride and silicon dioxide: i) the bath temperature which is normally a constant temperature at around 160°C and ii) the water content of the bath.

The water content of the bath varies because of the continous water evaporation due to the high temperature, the water evaporation during lid opening and the chemical reaction as indicated above. So far, a constant amount of water is continously spiked during the process, but this procedure is not

well controlled and the amount of spiked water is often determined empirically.

In order to maintain constant the water content in a phosphoric acid/water system used for silicon nitride etching, US patent No. 5 779 927 suggests an apparatus and a method, in which the liquid acid evaporant is condensed and returned to the main volume of the acid. In order to control the amount of pure water added, either the pH of the condensed evaporant is measured or, alternatively, the conductivity of the phosphoric acid/water system is measured.

However, these measurement mechanisms involve major structural changes of the etching apparatus. In particular, a special piping has to be attached to the apparatus in order to return the condensate via the pH meter to the acid bearing container.

It is therefore an object of the present invention to provide an improved apparatus and an improved method for the in-situ measurement of the water content of a hot liquid mixture which contains water.

Moreover, it is an object of the present invention to provide an improved apparatus and an improved method for the in-situ control of the water content of a hot liquid mixture which contains water.

According to the present invention, the above objects are achieved by the apparatus of claims 1 and 8 as well as the methods of claims 9 and 10, respectively.

The present invention provides an apparatus for measuring the water content of a water containing liquid mixture contained in a tank, comprising a heating device for controlling the temperature of said liquid mixture to a temperature near the boiling point of said liquid mixture, a cooling medium sys-

tem, disposed at the top of the tank, having a cooling medium inlet and a cooling medium outlet, a temperature measurement system for determining the temperature difference between cooling medium inlet and cooling medium outlet, and a computing device for calculating the water content of said liquid mixture from said temperature difference.

In addition, the present invention provides an apparatus for controlling the water content of a water containing liquid mixture comprising the apparatus for measuring the water content of a water containing liquid mixture as defined above, a tank for supplying water to said liquid mixture, and a control system for adjusting the amount of water supplied from the tank on the basis of the water content measured by said apparatus for measuring the water content.

Moreover, the present invention provides a method for measuring the water content of a water containing liquid mixture contained in a tank with a cooling medium system disposed at the top of the tight chemistry tank, said cooling medium system having a cooling medium inlet and a cooling medium outlet, comprising the steps of controlling the temperature of said liquid mixture to a temperature near the transition point of said liquid mixture, determining the temperature difference between cooling medium inlet and cooling medium outlet, and calculating the water content of said liquid mixture from said temperature difference.

Furthermore, the present invention provides a method for controlling the water content of a water containing liquid mixture comprising the steps of the method for measuring the water content of a water containing liquid mixture as defined above and the step of adjusting the amount of water supplied from a water supply tank on the basis of the measured water content.

The temperature of the liquid mixture is prefereably to be held constant.

The preferred embodiments are defined in the dependent claims.

The measurement principle underlying the present invention will be described with reference to a phosphoric acid/water system which is the water containing liquid mixture in the embodiment. However, the described apparatus and method can also be used with any other liquid mixture which contains water, which is held at a temperature near the boiling point of the liquid mixture.

As can be seen from Figure 3, the boiling point of phosphoric acid depends on the phosphoric acid concentration. Figure 3, which is taken from W. van Gelder, V. E. Hauser, J. Electrochem Soc., 114, 869 (1967), illustrates the dependence of the boiling point of phosphoric acid on the phosphoric acid concentration at a pressure of $1{,}013 * 10^5$ Pa.

The amount of evaporated water of a mixture at a constant temperature depends only on the concentration of water in the liquid mixture.

This water can be condensed back on cooling lids or a condensation line in general on top of the process tank, respectively. Since the lids are water cooled, the condensation is accelerated. The tank is preferably a tight chemistry tank. However, as the system is not a closed system there is a continous loss of evaporated water. Besides this, water is also consumed by the reaction described in Equation 1.

The basic idea underlying the present invention is to measure the temperature difference induced by the condensation rate $\Delta T(cr)$ between cooling water in- and outlet of the condensation line. At a constant flow and a constant temperature of

the cooling medium, the temperature difference between inlet and outlet of the cooling lines is dependent on the condensation rate:

$$\Delta T(cr) = T_2(cr) - T_1,$$

wherein $T_2(cr)$ denotes the temperature of the cooling medium outlet, and T_1 denotes the temperature of the cooling medium inlet.

The temperature difference $\Delta T(cr)$ is proportional to the amount of evaporated water mH_2O_{evap}. The amount of evaporated water is inversely proportional to ΔT_b. As shown in figure 3 ΔT_b is the difference between the controlled temperature of the current liquid mixture and the boiling point of the mixture at this concentration, therefore

$$\Delta T(cr) \sim mH_2O_{evap} \sim 1/\Delta T_b.$$

ΔTb is inversely proportional to the water concentration in the bath, therefore

$$\Delta Tb \sim 1/[H_2O_{bath}].$$

Accordingly, the following relation holds

$$\Delta T(cr) \sim [H_2O_{bath}].$$

For the purpose of the present invention, it is required that both the bath temperature and the cooling medium inlet temperature are maintained constant or at least temperature controlled allowing for temperature compensation. Moreover, the bath is held at a constant temperature near the boiling point of the liquid mixture, i.e. the boiling temperature ± 5 %.

This temperature difference signal of the cooling water system is fed to a computing device for calculating the water

content of said aqueous solution. The computing device uses an appropriate software which is able to compensate for temperature differences, for instance, when a lot is going into the process tank and the lids are open for a certain time.

The signal representing the calculated water content can be used to adjust the correct water spiking rate.

In summary, the apparatus and methods of the present invention provide the following advantages:

- The apparatus and methods of the present invention allow an in-situ control of the water content in HOT PHOS baths; accordingly the etching rate can exactly be adjusted and stabilized, moreover the life time of the bath and the quartz tank can be extended.
- The apparatus and method of the present invention can easily be installed. Only a temperature measurement system, a computing device as well as a control system for adjusting the amount of water supplied have to be attached to the normally used etching reactor. Accordingly, no big hardware changes are necessary.
- The apparatus and method of the present invention can easily be adapted to other spiking processes with condensation lines, the spiking processes running at a constant temperature.

The cooling medium used for the present invention can be any suitable cooling medium, for example water, an appropriate fluid or gas.

According to the present invention, the cooling medium system is arranged at the top of the process tank. According to an embodiment of the present invention, the cooling medium is housed in the lid of the process tank. In particular, the cooling medium can be implemented as a cooling coil comprising one or more loops in order to increase the condensing surface.

The invention increases the bath lifetime, since the concentration of the HOT PHOS bath is held within the optimum range. Further, product quality is increased by maintaining a constant etch rate over the bath lifetime.

In the following a preferred embodiment of the present invention will be described in detail.

Figure 1 illustrates an apparatus embodying the present invention, taken in a side view;
Figure 2 illustrates an example of the cooling medium system used in the present invention, taken in a plan view;
Figure 3 illustrates the dependence of the boiling point of phosphoric acid on the concentration of phosphoric acid.

In Figure 1 reference numeral 1 denotes the process tank housing the HOT PHOS bath 2 which in the present case is an approx. 86 % H_3PO_4 under well controlled processing conditions. During the etching process, for example, silicon wafers (not shown) partially coated with a silicon nitride layer, are immersed into the HOT PHOS bath 2. Reference numeral 3 denotes the water evaporated from the HOT PHOS bath. A heating device (not shown), for instance inline heaters, are provided in order to hold the HOT PHOS bath 2 at a constant temperature, which is in the present case near 160°C. The pressure inside the process tank 1 is at normal air pressure.

The process tank 1 is lid cooled by the cooling water system 4 having a cooling water inlet 5 and a cooling water outlet 6. The cooling water inlet 5 is held at a constant temperature T_1 which temperature is measured by a temperature sensor 11, and the temperature T_2 of the cooling water outlet 6 is measured by a temperature sensor 7. Control means (not shown) are provided in order to maintain a constant flow of the

cooling water across the cooling water system so that the heat is uniformly carried off. A controller 8 calculates the temperature difference between the outlet temperature T2 and the inlet temperature T1. The controller acts to hold the temperature constant in the steady state. In addition a flow meter (not shown) can be inserted at the inlet 5. The flow meter provides a signal to the computer 8 so that the system can process the amount of liquid flow.

As shown in Figure 2, the cooling water system can be divided into two symmetrical branches comprising a right lid 12 and a left lid 13. Each of the two branches is implemented as a cooling loop comprising one or more loops. The two symmetrical branches are joined at a junction point 14, and the temperature of the joined branches is measured by the temperature sensor 7. Of course, the cooling water system can also be divided into more than two symmetrical branches.

As can be seen from Figure 1, the temperature difference between cooling water inlet and outlet is given to the computer 8 which is provided with an appropriate software so that the water content of the HOT PHOS bath can be determined from this temperature difference.

A signal provided by the computer 8 is given to the valve 9 or a spiking pump which controls the water amount supplied by the water tank 10.

In the course of time, the water content of the HOT PHOS bath 2 will vary. In case the HOT PHOS concentration increases, less H_2O will be evaporated. Consequently the temperature difference between cooling water outlet and cooling water inlet will decrease, and the water spiking has to be increased. In case the HOT PHOS concentration decreases, more H_2O will be evaporated. Consequently the temperature difference between cooling water outlet and cooling water inlet will increase, and the water spiking has to be decreased.

Referring to figure 3 the dashed line represents the different possible states in the bath. Starting for instance, at a H_3PO_4 concentration of approximately 81 wt-% (marked as A) the desired temperature of 160 °C can not be reached until the water concentration is reduced by boiling to the relating point of B.

Van Gelder and Hauser, J. Electrochem. Sec., 114, 869 (1967) reported that the vapor phase in equilibrium with phosphoric acid is virtually pure water up to temperatures of 250 °C. Assuming a bath at a constant temperature of 160 °C without spiking possibility, mainly the water concentration is permanently decreased in direction to reference point C due to the fact that the system is an open system.

In case of water spiking the concentration of water is held nearly constant and the state in the bath is always between B and C close to point B. As mentioned above, ΔT_b is the temperature difference between the controlled temperature of the current liquid mixture and the boiling point of the mixture at a given concentration between B and C.

Claims

1. Apparatus for measuring the water content of a water containing liquid mixture (2) contained in a tank (1), comprising:
- a heating device for controlling the temperature of said liquid mixture (2) to a temperature near the boiling point of said liquid mixture (2);
- a cooling medium system (4), disposed at the top of the tank (1), having a cooling medium inlet (5) and a cooling medium outlet (6);
- a temperature measurement system (7) for determining the temperature difference between cooling medium inlet (5) and cooling medium outlet (6); and
- a computing device (8) for calculating the water content of said liquid mixture (2) from said temperature difference.

2. Apparatus for measuring the water content of a water containing liquid mixture (2) according to claim 1, wherein said liquid mixture (2) is an acid/water system.

3. Apparatus for measuring the water content of a water containing liquid mixture (2) according to claim 2, wherein said acid is phosphoric acid.

4. Apparatus for measuring the water content of a water containing liquid mixture (2) according to any of the preceding claims, wherein said cooling medium inlet (5) is held at a constant temperature.

5. Apparatus for measuring the water content of a water containing liquid mixture (2) according to any of the preceding claims, wherein said cooling medium is water.

6. Apparatus for measuring the water content of a water containing liquid mixture (2) according to any of the preceding

claims, wherein said cooling medium system (4) is housed in the lid of the tank (1).

7. Apparatus for measuring the water content of water containing liquid mixture (2) according to any of the preceding claims, wherein said cooling medium system (4) is divided into two or more symmetrical branches each comprising one ore more loops.

8. Apparatus for controlling the water content of a water containing liquid mixture (2) comprising:
- the apparatus for measuring the water content of a water containing liquid mixture (2) according to any of claims 1 to 7;
- a tank (10) for supplying water to said liquid mixture (2); and
- a control system (9) for adjusting the amount of water supplied from said tank (10) on the basis of the water content measured by said apparatus for measuring the water content.

9. Method for measuring the water content of a water containing liquid mixture (2) contained in a tank (1) with a cooling medium system (4) disposed at the top of the tank (1), said cooling medium system (4) having a cooling medium inlet (5) and a cooling medium outlet (6), comprising the steps of:
- controlling the temperature of said liquid mixture (2) to a temperature near the boiling point of said liquid mixture;
- determining the temperature difference between cooling medium inlet (5) and cooling medium outlet (6); and
- calculating the water content of said liquid mixture (2) from said temperature difference.

10. Method for controlling the water content of a water containing liquid mixture (2) comprising the steps of the method for measuring the water content of a water containing liquid mixture (2) of claim 9 and the step of adjusting the amount

of water supplied from a water supply tank (10) on the basis of the measured water content.

FIG 1

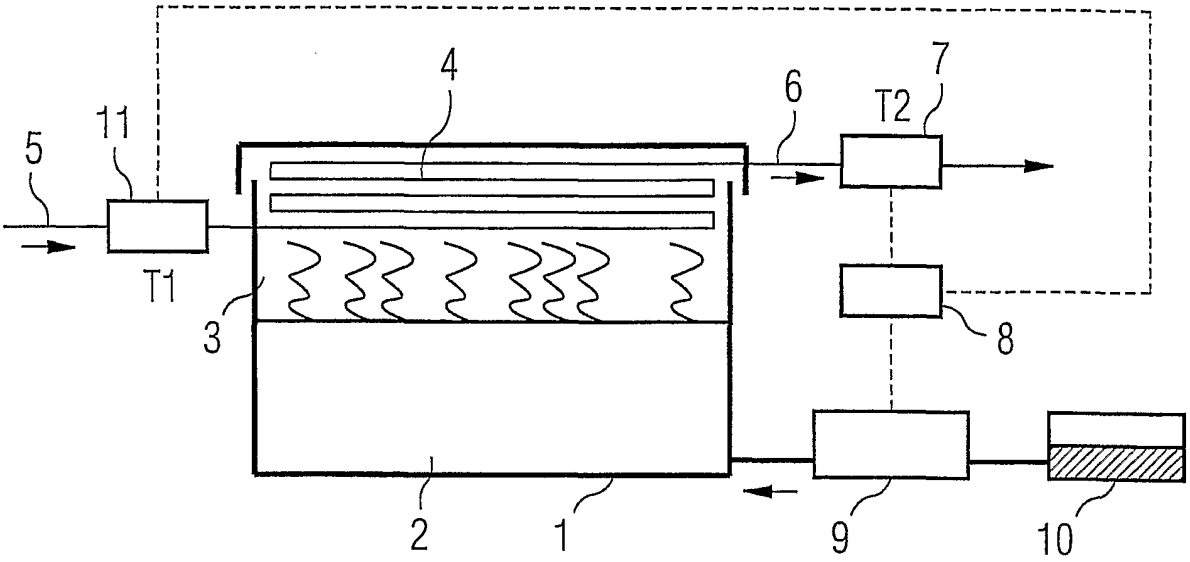


FIG 2

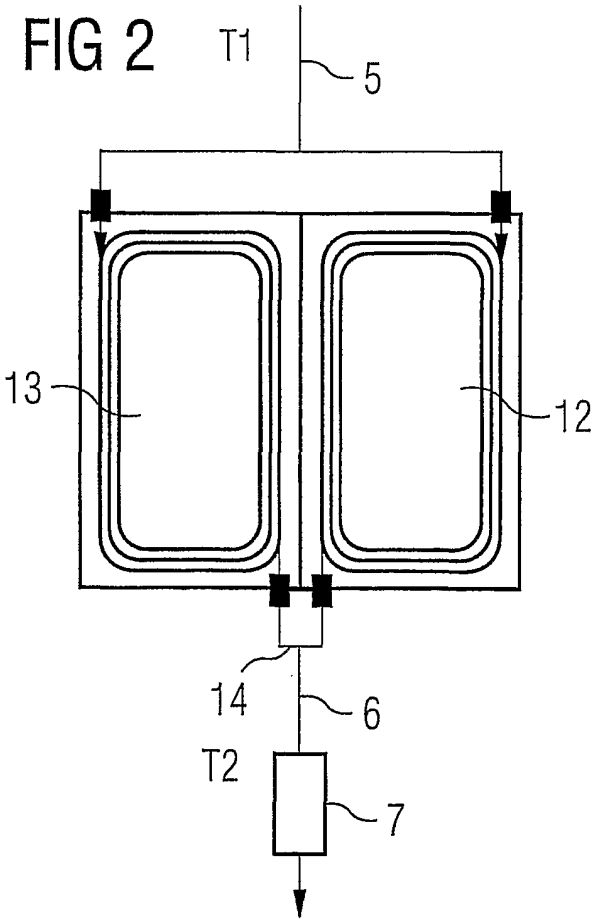
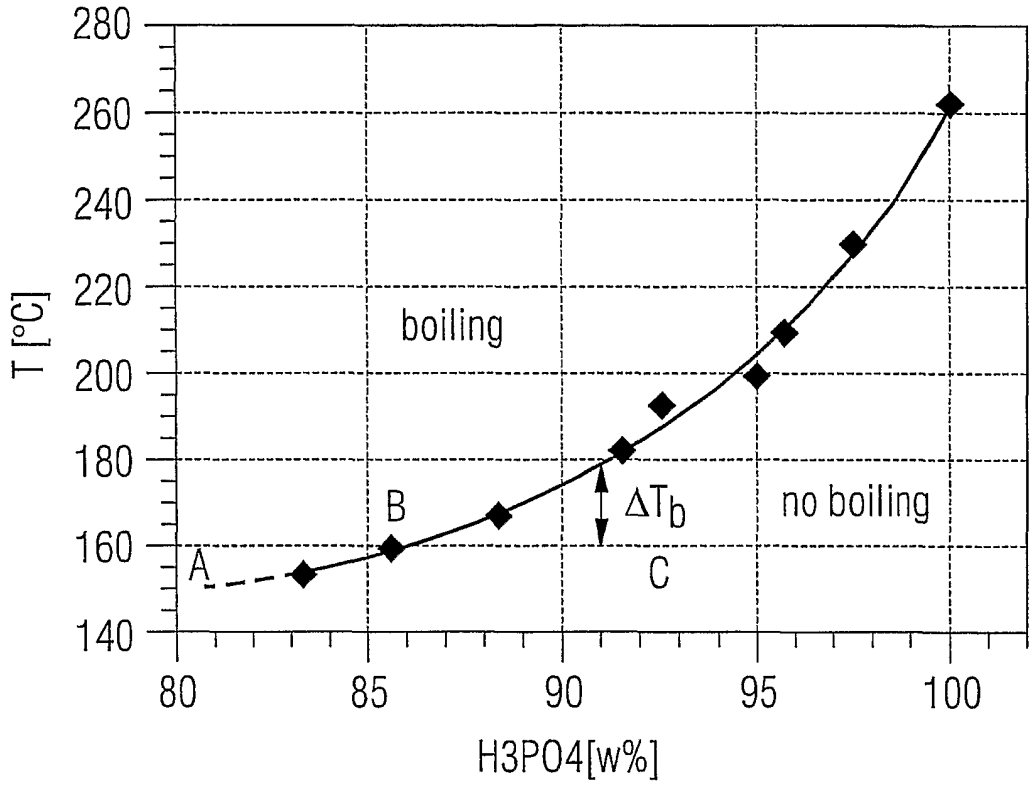


FIG 3


280
260
240
220
200
180
160
140
T [°C]
boiling
B
A
ΔTb
C
no boiling
80
85
90
95
100
H3PO4[w%]

INTERNATIONAL SEARCH REPORT

Int nal Application No
PCT/EP 01/10188

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N25/14 G01N25/56

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)
IPC 7 G01N H01L

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 779 927 A (LO CHI-HSIN) 14 July 1998 (1998-07-14) cited in the application the whole document	1-3,5,6, 8-10
A	US 5 938 885 A (HUANG CHENG-CHUNG ET AL) 17 August 1999 (1999-08-17) abstract; figure 3	1-3,8-10
A	EP 0 474 482 A (FUJITSU LTD) 11 March 1992 (1992-03-11) the whole document	1-3,8-10
A	EP 0 508 212 A (GOODYEAR TIRE & RUBBER) 14 October 1992 (1992-10-14) abstract column 9, line 4-19; figure 1	1,8-10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
2 January 2002	14/01/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Meyer, F

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INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/EP 01/10188

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 766 553 A (KEYES IV MARION A ET AL) 23 August 1988 (1988-08-23) abstract	1,9

1

INTERNATIONAL SEARCH REPORT

formation on patent family members

Int al Application No
PCT/EP 01/10188

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