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(71) Applicant: **POLITECNICO DI MILANO** [IT/IT]; Piazza Leonardo Da Vinci, 32, 1-20133 Milano (IT).

(72) Inventors: **BONALUMI, Davide;** c/o Politecnico Di Milano, Piazza Leonardo Da Vinci, 32, 1-20133 Milano (IT). **MACCHI, Ennio;** c/o Politecnico Di Milano, Piazza Leonardo Da Vinci, 32, 1-20133 Milano (IT). **LASALA, Silvia;** c/o Politecnico Di Milano, Piazza Leonardo Da Vinci, 32, 1-20133 Milano (IT).

(74) Agent: **RIGAMONTI, Dorotea** et al; c/o Jacobacci & Partners S.p.A., Via Senate, 8, 1-20121 Milano (IT).

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**(54) Title:** $CO_2$-BASED MIXTURES AS WORKING FLUID IN THERMODYNAMIC CYCLES

**(57) Abstract:** The present invention relates to a working fluid for a thermodynamic cycle which comprises CO2 as main component and one or more of the compounds selected from the group which comprises: T1CI4, TiBr4, SnCU, SnBr4, VCI4, VBr4, GeCU, metal carbonyls, by way of example Ni(CO) 4.

# Description

"C02-based mixtures as working fluid in thermodynamic cycles "

The invention relates to the field of electric energy and, possibly, thermal energy generation. A new mixture to be used as working fluid is described, which fluid comprises CO2 as the major component, mixed with one or more of the compounds selected from T1CI4, TiBr4, SnCl4, SnBr4, VCI4, VBr4, GeCl4, metal carbonyls, by way of example Ni(CO)4. The mixture suggested here as a working fluid allows a greater thermodynamic cycle efficiency with respect to that which can be obtained with the use of CO2 alone.

## Prior art

Water is the preeminent working fluid used in closed cycles thermodynamic, in particular in the Rankine Cycle.

The thermodynamic conversion of heat from non-traditional sources (geothermal energy, biomass energy, solar thermal energy, energy recovered from industrial processes) displays a great variety of interested powers, as well as different heat sources (liquid, gas, mixtures of gases and vapors), making the conventional steam and gas cycles inadequate. For this reason, an intense search is underway for working fluids alternative to water which allow the implementation of different and appropriate thermodynamic cycles, whereby guaranteeing the operating conditions for efficient conversion for any power size or temperature level.

Organic fluids are advantageously used in thermal recovery from industrial processes. For example, WO2007033958 describes perf luorocarbons and/or polyethers perfluorates and/or ketones perfluorates as working fluids for thermodynamic cycles. Said organic fluids are used at maximum temperatures up to 400°C. The limited thermal stability of organic fluids makes use at temperatures higher than 350-400°C impossible.

$CO_2$ has been experimentally tested with the objective of operating in thermodynamic cycles at temperatures equal to or higher than 400°C. $CO_2$ has a critical temperature of about 31°C and a corresponding critical pressure of about 73 bar. These properties imply the cycles known as Joule-Brayton cycles as the main use of such fluid. Typically, by adopting a compressor to increase the pressure of the fluid itself, which is in the gaseous phase, they make its use for cycles at limited maximum temperatures energetically unfavorable.

$CO_2$~based mixtures have been suggested with the objective of allowing use in Rankine cycles, but these have proven to be of little use, because of their thermal instability. For example, CN103937459B describes a mixture based on $CO_2$ which also includes either propane, cyclopropane, propene, butane, iso-butane, cis-butene, trans-butene or cyclopentane . The critical temperature is improved (raised) but the additional components have poor thermal stability, whereby making the mixture not applicable to thermodynamic cycles which reach temperatures of 400°C and beyond.

$CO_2$ and benzene mixtures have also been suggested, with more favorable critical temperatures and with a high thermal stability but with disadvantages linked to the carcinogenicity of benzene.

T1CI4 is an important intermediate in the production of metallic titanium and T1O2, which is liquid at ambient temperature. Typically, T1CI4 is isolated from mixtures which comprise it by means of distillation. Tolley WK et al. (Metallurgical Transactions B, Titanium tetrachloride-supercritical carbon dioxide interaction: A solvent extraction and thermodynamic study, 1992, Volume 23 (1) :65-72) alternatively suggest the removal of T1CI4 from AICI3 mixtures with supercritical $CO_2$ .

The need for new working fluids, which are liquid at ambient temperature and have high thermal stability, is strongly felt.

## Description of the invention

The present invention relates to a mixture which comprises $CO_2$ as main component and one or more of the compounds selected from the group which comprises: T1CI4,

$TiBr_4$, $SnCl_4$, $SnBr_4$, $VC1_4$, $VBr_4$, $GeCl_4$, metal carbonyls, by way of example $Ni(CO)_4$.

Description of the figures

**Figure 1**: Efficiency of a thermodynamic cycle at temperatures between 400 and 700°C using as working fluid either CO2 (dashed line) or a mixture which comprises CO2 and $TiCl_4$ 2.5 mol% (solid line) .

**Figure 2**: Efficiency of a thermodynamic cycle at temperatures between 300 and 700°C using as working fluid either CO2 (dashed line) or a mixture which comprises CO2 and $TiCl_4$ 2.5 mol% (solid line), or $C0_2$ and $TiCl_4$ 10 mol% (solid bold line) .

**Figure 3**: Diagram of a regenerative system which uses a mixture according to the present invention as a working fluid .

Detailed description of the invention

The mixture which is the object of the present invention comprises CO2 as main component and one or more of the compounds selected from the group which comprises: TiC14, TiBr4, SnC14, SnBr4, VC14, VBr4, GeC14, metal carbonyls, by way of example $Ni(CO)_4$.

In a preferred embodiment, said mixture comprises CO2 and one of the compounds selected from the group which comprises: TiC14, TiBr4, SnC14, SnBr4, VC14, VBr4, GeC14, metal carbonyls, by way of example $Ni(CO)_4$.

In a further embodiment, said mixture comprises $CO_2$ and one of the compounds selected from the group which comprises: TiC14, TiBr4, SnC14, SnBr4, VC14, VBr4, GeC14, GeC14 .

Said additional compound is present in the mixture of $CO_2$ with a concentration comprised between 1 and 30 mol%, or between 2 and 20 mol%, or between 2.5 and 10 mol% .

In a preferred embodiment, the mixture according to the present invention consists in $CO_2$ and one of the compounds selected from the group which comprises: T1CI4, TiBr4, SnCl4, SnBr4, VCI4, VBr4, wherein said additional compound is present at a concentration comprised between 1 and 30 mol%, or between 2 and 20 mol%, or between 2.5 and 10 mol%.

Said additional compound is added to the mixture according to the present invention as a pure compound in 98%, or 99%, or 99.5% by weight. In a preferred embodiment, the compound is added with a purity of 99.9% by weight, preferably 99.99%, even more preferably 99.9999%. The high degree of purity guarantees the absence of impurities which may have a low thermal stability and cause, at high processing temperatures, undesired and even violent reactions, such as for example explosions.

In a particularly preferred embodiment, said additional compound is $TiCl_4$.

$TiCl_4$, $TiBr_4$, $SnCl_4$, $SnBr_4$, $VC1_4$, $VBr_4$ can be mixed with the liquid $CO2$ and surprisingly elevate its critical temperature, leading to a surprising advantage in terms of efficiency when the mixtures according to the present invention are employed in thermodynamic cycles which operate at temperatures equal to higher than 400°C.

The mixture according to the present invention has the surprising advantage of significantly modifying the critical temperature of the $CO2$, whereby obtaining a fluid which is liquid up to 40°C, or up to 50°C, i.e. higher than 31°C. Furthermore, the mixture obtained is thermodynamically stable and is able to withstand operating temperatures of 400°C and higher without significant alterations and without originating undesired degradation products, increasing operational efficiency of thermodynamic cycles in which it is used as working fluid in replacement of $CO2$ as such.

The advantage in terms of operational efficiency recovery in thermodynamic cycles has been found to be particularly significant with mixtures which comprise concentrations higher than 2 mol% of compound. The advantage tends to be imperceptible to concentrations close to 40 - 50 mol% of compound. For each concentration, as the temperature increases, in particular at temperatures higher than 700°C, we have hereby demonstrated that the difference in efficiency between a thermodynamic cycle operating with pure $CO_2$ and a thermodynamic cycle operating with a mixture according to the present invention tends to be lower, while maintaining a non-insignificant advantage for the mixture.

By way of example, figure 1 shows the performance of a thermodynamic cycle operating with a mixture of $CO_2$ and T1CI4 2.5 mol% (solid line) and the performance of the same operating cycle with pure $CO_2$ (dashed line) . The mixture shows higher performance at all temperatures, at 400°C the performance increase is greater than the increase observed at higher temperatures.

An increase in the concentration of the compound leads to better performance, but increments are greater at low molar concentrations (2-5%) . An excessive increase of the concentration of the compound causes slightly better performance, with the disadvantage of operating with a greater amount of substance which is less easy to manage than $CO_2$ .

By way of example, figure 2 shows an example of comparison between the performance of a thermodynamic cycle operating with a mixture of $CO_2$ and T1CI4 10 mol% (solid bold line), with a mixture of $CO_2$ and T1CI4 2.5 mol% (solid line) and with pure $CO_2$ (dashed line) . It may be noted from the comparison between the solid bold line and the solid line, that the increase in performance is less evident as the concentration of TiC14 in the mixture increases .

It is particularly interesting to observe that the advantages in terms of efficiency were observed at relatively low compound concentrations, between 2 and 5 mol%. This is particularly significant because it allows the use of $CO_2$ mixtures with minimal additions of one of the indicated compounds. The toxicity, although limited, of the added compounds in the $CO_2$ mixture and their cost compared to the cost of $CO_2$ have very limited impact because of the small volumes used.

The performance of the thermodynamic cycles to which reference is made in the examples were evaluated by calculating the thermodynamic properties of the mixture. Cubic Peng-Robinson was used as thermodynamic equation; the equation parameters were inferred from experimental data .

The mixture according to the present invention is prepared according to methods known to a person skilled in the art. By way of example, the amount of one or more of the compounds to be added to the $CO_2$ is introduced in an anhydrous tank and flushed with an inert gas, such as $N_2$ or He. Said tank is connected to a $CO_2$ bottle, at a pressure higher than the final pressure of the tank, whereby obtaining the desired mixture.

The mixture according to the present invention is validly applied as working fluid in systems for the generating electric and possibly even thermal energy. It is also an alternative to fluids commonly used in ORC systems and in refrigeration systems.

By way of example, it may be used in electric and thermal energy generation and distribution, in organic fluid Organic Rankine Cycle engines (ORC), in co-generative engines and in refrigeration systems.

The mixture according to the present invention is advantageously used in geothermal heat systems, solar heat systems, in particular solar towers, in waste incinerators or biomass systems. Advantageously, the mixture according to the present invention is used in aerospace applications .

Figure 3 diagrammatically shows, by way of example, a regenerative system operated with the mixture according to the present invention. The system (1) comprises a circuit (2) in which the mixture according to the present invention circulates. Said circuit (2) comprises two exchange points with the outside environment, a heat exchanger (3) which acquires heat from the outside and a condenser (4) which exchanges heat with the environment to obtain saturated liquid. Said mixture is circulated in said circuit (2) by a pump (5). Since said mixture is in liquid state, the circuit is operated by a pump and not by a compressor, which requires higher energy costs for operation. Having acquired heat from the heat exchanger, the mixture actuates a turbine (6) which generates the energy after its crosses a recuperator (7) . The passage in the recuperator (7) exchanges heat between the mixture exiting from the turbine and the mixture entering into the primary heat exchanger, whereby allowing a recovery of the remaining heat, as well as a lowering of the temperature of the mixture before it enters into the condenser. From the recuperator, the mixture flows into the condenser (4), in which it condenses and resumes the cycle .

Advantageously, the solution suggested in the present invention, by replacing the $CO_2$ with a mixture having a critical temperature greater than the $CO_2$, makes it possible to have the same mixture in liquid phase also at temperatures higher than the critical value of $CO_2$, wherein said mixture is in a liquid phase even at temperatures of 50°C, or 40°C. The mixture according to the present invention, makes it possible to have a working fluid in liquid phase, whereby permitting the adoption of the Rankine cycle, in which the compression phase occurs advantageously by using a pump and not a compressor.

T1CI4 is particularly advantageous since it is an intermediate synthesis product. The product is therefore available at an affordable price.

# CLAIMS

1. A working fluid for a thermodynamic cycle which comprises CO2 as main component and one or more of the compounds selected from the group which comprises: $TiCl_4$, $TiBr_4$, $SnCl_4$, $SnBr_4$, $VC1_4$, $VBr_4$, $GeCl_4$, metal carbonyls, by way of example $Ni(CO)_4$.

2. A working fluid for a thermodynamic cycle according to claim 1, which comprises CO2 and one of the compounds selected from the group which comprises: $TiCl_4$, $TiBr_4$, $SnCl_4$, $SnBr_4$, $VC1_4$, $VBr_4$ $GeCl_4$, $GeCl_4$, metal carbonyls, by way of example $Ni(CO)_4$.

3. A working fluid for a thermodynamic cycle according to claim 1 or 2, wherein said compound is added with a concentration comprised between 1 and 30 mol%, or between 2 and 20 mol%, or between 2.5 and 10 mol%.

4. A working fluid for a thermodynamic cycle according to any one of claims from 1 to 3, wherein said additional compound is added as a pure compound in 98% by weight, or at purities higher than 99% or 99.5%.

5. A working fluid for a thermodynamic cycle according to any one of claims from 1 to 4, wherein said additional compound is added with a purity of 99.9% by weight, preferably 99.99%, even more preferably 99.9999%.

6. A working fluid for a thermodynamic cycle according to one of claims from 1 to 5, wherein said additional compound is $TiCl_4$.

7. A process for converting thermal energy, preferably of fossil, biomass, solar, geothermal, process heat origin, into mechanical and/or electric energy, wherein a working fluid is employed according to one of claims 1 to 6.

8. A system for operating a conversion process from thermal energy to mechanical and/or electric energy, wherein the working fluid used is a working fluid according to one of claims from 1 to 6.

9. A system according to claim 8, wherein said thermal energy is obtained from solar towers.

Efficiency for 2.5 mol% with recovery system layout

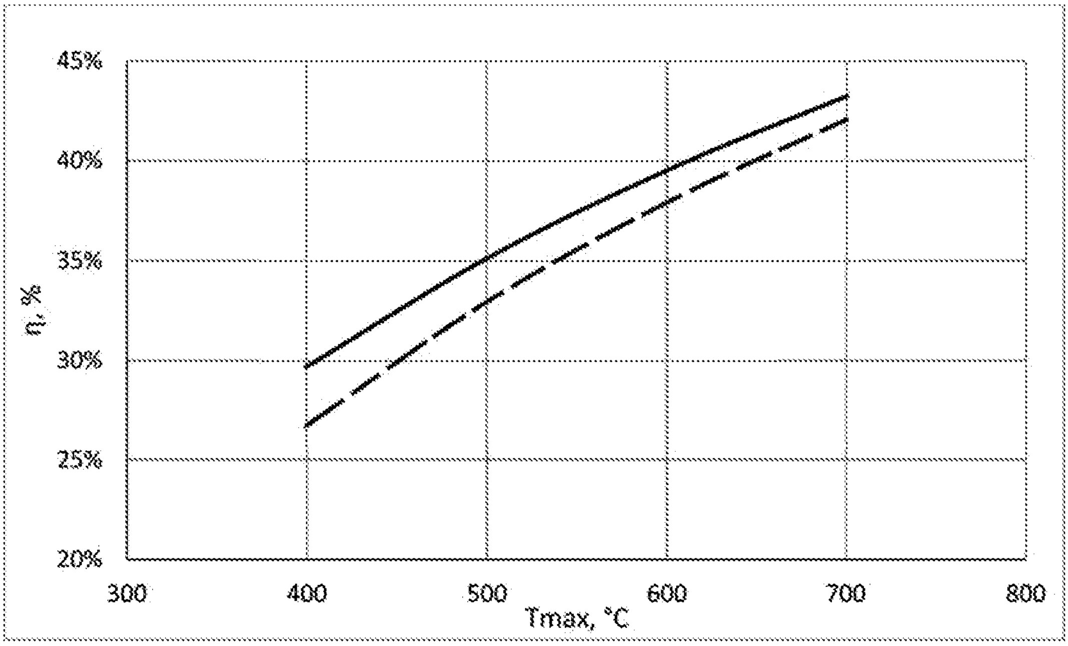


FIG. 1

Efficiency for 0 mol%, 2.5 mol%, 10 mol% with recompressed layout

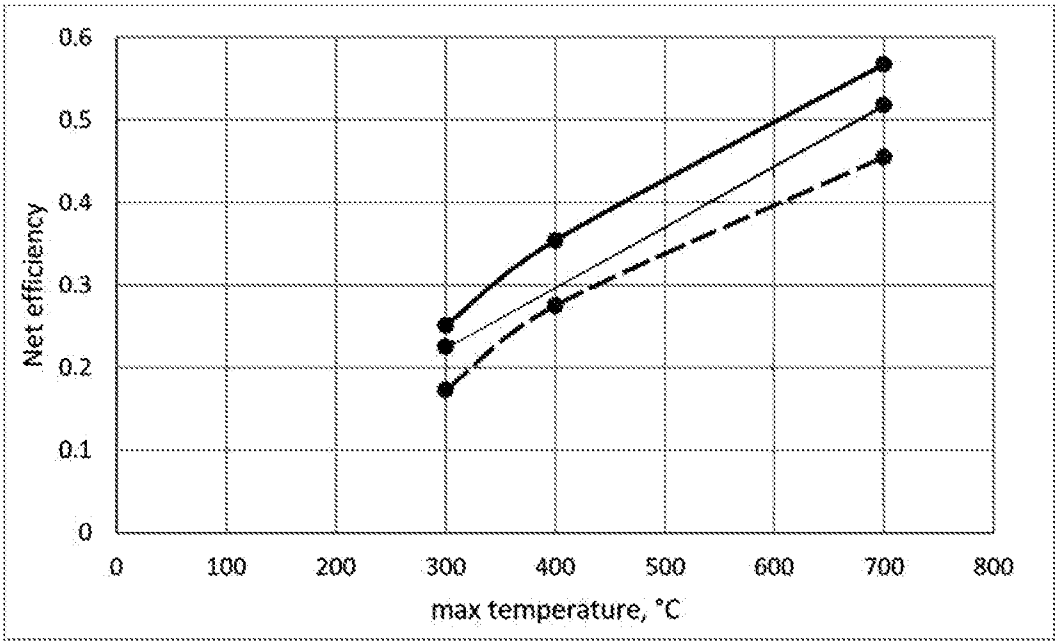


FIG. 2

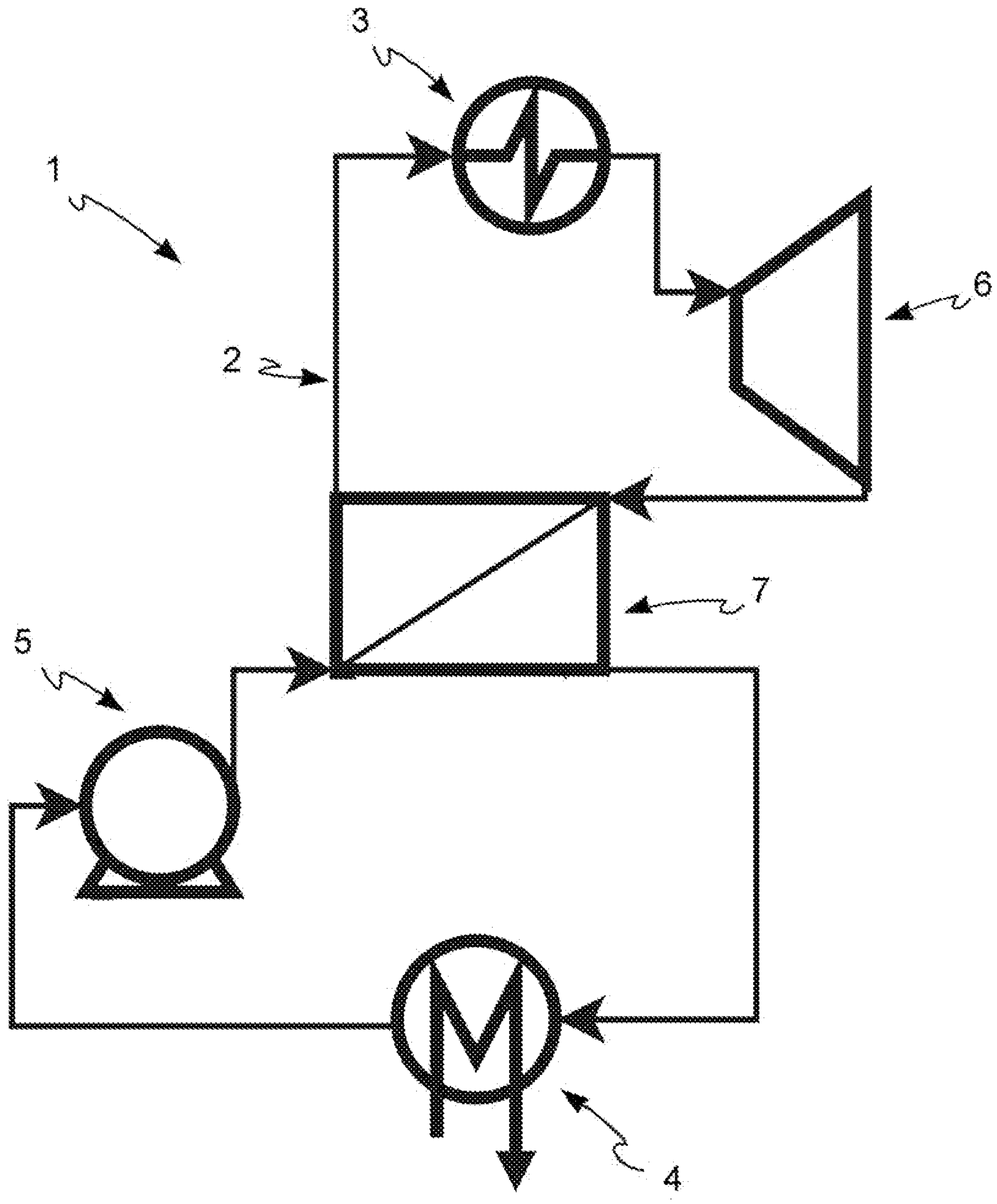


FIG. 3

# INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/056719

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K5/04 F01K25/00
ADD.

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)
C09K F01K F22G

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 practicable, search terms used)

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 2009/107144 A1 (MOGHTADERI BEHDAD [AU] ET AL) 30 April 2009 (2009-04-30)<br>the whole document<br>----- | 1-9 |
| A | TOLLEY W K ET AL: "TITANIUM TETRACHLORIDE-SUPERCRITICAL CARBON DIOXIDE INTERACTION: A SOLVENT EXTRACTION AND THERMODYNAMIC STUDY",<br>METALLURGICAL TRANSACTIONS B. PROCESS METALLURGY, METALLURGICAL SOCIETY OF AIME. NEW YORK, US,<br>vol. 23B, no. 1,<br>1 February 1992 (1992-02-01), pages 65-72, XP000270940,<br>cited in the application<br>the whole document<br>----- | 1-9 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
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| 13 December 2018 | 04/01/2019 |

| Name and mailing address of the ISA/ | Authorized officer |
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| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Puetz, Christine |

1

# INTERNATIONAL SEARCH REPORT

**Information on patent family members**

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