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[Continued on next page]

(54) **Title:** PROCESS AND APPARATUS FOR THE THERMAL TREATMENT OF CONTAMINATED SOLIDS

(57) Abstract: Process and Apparatus for the Thermal Treatment of Con-

Contaminated Solids The invention relates to a thermal treatment of contaminated solids. In a first step (i) the contaminated solids are preheated in at least one preheating stage to a temperature between 100 and 600°C by counter-current-flow with a heat-transfer medium. In a second step (ii) the contaminated solids then are heated in a first reactor to a temperature between 600 and 1300 °C, whereby the impurities contained in the solids are partly driven out in gaseous form and an off-gas is obtained. By a third step (iii) the solids are thermally treated in a second reactor at a temperature between 600 and 1300 °C, whereby impurities contained in the solids are driven out in gaseous form and in the fourth step (iv), the off-gases are recirculated as heat-transfer medium and/or combustion air into the at least one preheating stage.

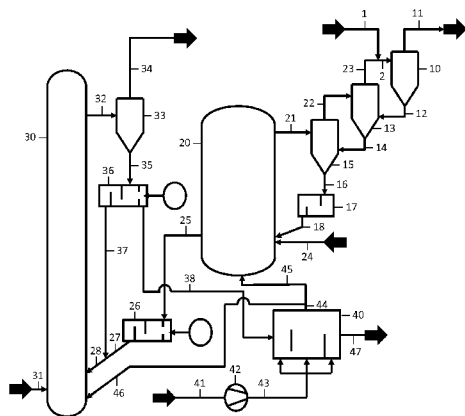


Fig. 1



SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG). **Published:**

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Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Process and Apparatus for the Thermal Treatment of Contaminated Solids

This invention relates to a process and an apparatus for the thermal treatment of contaminated solids, comprising a step (i) for preheating the solids in at least one preheating stage to a temperature between 100 and 600 °C with a heat-transfer medium, a step (ii) for heating the solids in a first reactor to a temperature between 600 and 1300 °C, whereby the impurities contained in the solids are partly expelled in gaseous form and a waste gas is obtained, a step (iii) directed to a thermal treatment of the solids in a second reactor at a temperature between 600 and 1300 °C, whereby impurities contained in the solids are at least partly driven out in gaseous form and a step (iv) routing of the off-gas into the at least one preheating stage as heat-transfer medium.

The thermal treatment of solids to remove impurities is known from a plurality of processes, such as e.g. the thermal decontamination of contaminated soils or the high-temperature degasification of coals and petroleum coke. The heating of solids in the usual temperature range between 600 and 1300 °C however is very energy-intensive. An optimum energy recovery from the waste gases involved in these processes therefore is essential for the economy of such processes.

Thermal treatments to remove impurities from solids, however, have the additional disadvantage that at least a part of the contained impurities is evaporated and thus passes over into the off-gas of the thermal treatment. The simplest recovery of the sensible heat of the formed off-gas by direct counter-current-flow and direct contact of the material to be preheated with the off-gas, as it is known from the usual thermal treatments, e.g. calcining, therefore is not possible: Since the impurities set free at high temperatures into and contained in the off-gas, it would occur in this case that during the counter-current-flow for preheating purposes the impurities contained in the off-gas again attach to the still compar-

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actively cold solids by physical and chemical processes. The previously thermal-ly cleaned solids hence are again contaminated due to the resorption of the pollutants released. When it then is guided into the actual thermal treatment, the same hardly is suited to produce the necessary degree of purity due to the
5 remaining impurity. Moreover, in a continuous process an extreme accumulation of impurities occurs in a very short time.

An indirect heat utilization of the heat contained in the off-gas however involves a distinctly worse thermal efficiency due to the heat-exchange surface limited for
10 economic reasons and thus diminishes the energetic economy of the process. In addition, the required equipment is distinctly more cost-intensive in terms of both acquisition and maintenance.

It therefore is the objective underlying the invention to provide a process which
15 provides for removing impurities from solids by a thermal treatment in an energetically optimized way.

This objective is solved by a process with the feature of claim 1.

20 For this purpose, the contaminated solids initially are preheated in a process step (i) in at least one preheating stage in direct contact with the waste gas to a temperature between 100 and 600 °C, preferably however to a temperature which allows a largely technically expedient utilization of the sensible heat of the combustion gas released. As a result, there is a direct heat transfer between the
25 heat-transfer medium off-gas and the solids to be heated, whereby in particular in a multistage heat exchange a high thermal efficiency is achieved. Subsequently, the solids preheated in this way are preheated in a first reactor to a temperature between 600 and 1300 °C, preferably 600 to 1200 °C, even more preferred 750 to 1000 °C, and the gaseous impurities contained therein are
30 partly driven out, whereby an off-gas is obtained. The so operated first process

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stage allows for the recovery of the bulk of the sensible heat contained in the combustion off-gas.

According to the invention, the off-gas is supplied as heat-transfer medium to a preheating stage, where it gets in direct contact with the solids by counter-current-flow with the same. The so preheated solids are further increased in temperature in the first reactor by means of the combustion of a gaseous or liquid fuel. The solids preheated in the first reactor are discharged to the second reactor where, the hot solids subsequently – depending on the solids temperature achieved in the first process step – are either kept at that particular temperature or further heated (in a second reactor) to a temperature between 600 and 1300 °C, whereby impurities still contained are driven out in gaseous form. Due to the fact that the off-gas stream of the second reactor – is of a comparatively small quantity – may no longer be thermally utilized and the pollutants contained therein are not resorbed again on the solids now purified.

This has the advantage that the expulsion of the impurity only partly must take place in the first reactor, but to a large extent is shifted into the second reactor. An accumulation of the impurity to be eliminated thereby is prevented just like it can be ensured that the solids in the end have a sufficient degree of purity. At the same time, there is also provided the advantage of a direct heat transfer from off-gas from the first reactor in the preheating stage, which is why the process can be operated distinctly more efficiently in energetic terms. The use of a second reactor does not lead to a heat requirement greatly increased again at this point, as in the first reactor already the contaminated material has been brought to the temperature required for the expulsion of the impurity and possibly proceeding endothermal processes already are covered here in energetic terms. Thus, the heat quantity which must be applied in the second reactor, and hence the amount of off-gas produced, is relatively small.

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Advantageously, preheating consists of at least two preheating stages. It is particularly favorable when the off-gas from the first reactor is guided in counter-flow to the solids to be heated, as thus a high energy transfer is achieved with low investment costs at the same time.

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Furthermore, it turned out to be favorable when heating in the first and - if not to be operated under a reducing atmosphere - in the second reactor is effected at an oxygen content between 1 and 20 vol-%, preferably 1 to 15 vol-%, particularly preferably 1 to 5 vol-%. This has the advantage that due to the reduced supply of oxygen as compared to an atmosphere of air fuel economy is enhanced and potentially less undesired side reactions can occur. However, if fuel is burnt within the reactor, in order to provide the energy required there, sufficient oxygen must be present at least in the first reactor for this combustion process.

15 The second reactor, in which the product finally is purified, in particular should be operated with an oxygen content which creates an optimum atmosphere for the removal of impurities. This can be an oxidizing or also a reducing atmosphere. Since the solids here enter already with relatively high temperature, preferably the temperature finally to be established in the second reactor, the amount of heat to be introduced by direct or indirect combustion here also is much smaller in general, which is why this does not require an excessively high oxygen content in the case of direct combustion and an oxidizing atmosphere. Preferably, step (ii) takes place in oxidizing atmosphere while step (iii) is performed with reducing atmosphere.

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Furthermore, it turned out to be favorable to achieve heating in the first and/or in the second reactor by supplying a preferably liquid or gaseous fuel, as in this way a uniform heat distribution can be ensured within the reactor.

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At the same time, however, it can also be advantageous to achieve heating in the first and/or the second reactor, above all in the second reactor, by supplying a hot gas, as then no oxygen is required within the reactor for the combustion of the supplied fuel and the reaction control thus is possible with very low oxygen content or under complete oxygen exclusion.

A further advantageous aspect of the invention provides that the material to be purified is cooled after passing the second reactor, wherein a gas, preferably air, likewise is used for cooling. The gas heated by cooling subsequently can be introduced into the preheating stage and/or the first and/or the second reactor, whereby this energy is utilized as well. The energy efficiency of the process thereby can be increased further.

For example – but not restricted to - the described process can easily be utilized for phosphate-containing solids, in which impurities typically are driven out by a thermal treatment. In particular sedimentary raw phosphates are impaired with regard to the further processing to and the utilization as fertilizer both by carbonate compounds and by comparatively high cadmium contents, which can be removed by the process described here. At the same time, the process also is suitable for phosphate-containing secondary raw materials whose impurities can be reduced or even be eliminated with the described process steps.

Furthermore, the described process can be used particularly well in solids having a cadmium content between 1 and 500 ppm, preferably 5-300 ppm, as cadmium (Cd) safely can be removed from the solids by a thermal treatment. The effect of the process on ores is not only limited to cadmium, but includes all substances which can be volatilized or decomposed by action of high temperatures and defined atmospheres, such as e.g. arsenic, to name only one impurity out of many.

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In detail, a phosphate containing material with a cadmium content require a first reactor with oxidizing atmosphere and a second one with reducing atmosphere (most preferred $O_2 = 0$ wt.-%) to remove contained cadmium. Therefore, a recycling of off-gases to previous process step is not desirable since it would lead to cadmium accumulation.

Furthermore, it turned out to be advantageous when the first and/or the second reactor is operated as fluidized-bed reactor with a stationary or a circulating fluidized bed, wherein here any combination is conceivable. A fluidized-bed reactor offers the advantage of a particularly good mass and heat transfer. At the same time, the process according to the invention in particular is expedient in a fluidized bed, as due to the fluidizing gases an intensive intermixing of the gas and solids phases is ensured with the result of a very uniform temperature distribution.

It also is advantageous to introduce spheres preferably of an inert and temperature resistant material into the reactor(s) designed as fluidized-bed reactor(s), which have a diameter between 5 and 50 mm. In particular when a reducing atmosphere is to be produced, a completion of the required partial oxidation could be achieved thereby to a large extent.

Furthermore, the invention also comprises an apparatus with the features of claim 11.

Such apparatus includes at least one preheating stage for preheating the solids to a temperature between 100 and 600 °C, preferably by counter-current-flow, with a heat-transfer medium.

Furthermore, it comprises a first reactor for heating the solids to a temperature between 600 and 1300 °C, whereby impurities contained in the solids are partly

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driven out in gaseous form and an off-gas is obtained. Furthermore, the apparatus includes a return conduit from the first reactor, through which the off-gas is introduced into the preheating stage as heat-transfer medium, and a second reactor, in order to further thermally treat the solids at a temperature between
5 600 and 1300 °C, so as to expel impurities in gaseous form.

It also is conceivable that in one apparatus the first and/or the second reactor are designed as rotary kiln.

10 Furthermore, an advantageous aspect of the invention provides that the at least one preheating stage is designed as cyclone.

The solids residence times required for the various chemico-physical processes taking place in the two reactors depending on the intended use can optimally be
15 adjusted both by the chosen geometry (construction) and by bed heights or bed densities variable in operation. Further, a two separate reactor design for different atmosphere, especially a first reactor with oxidizing atmosphere and a second reactor with reducing atmosphere, are preferred.

20 The first reactor typically hands over the solids to the second reactor preferably with that temperature with which the second reactor is to be operated. In the normal case, this results in minimum of energy to be expended. Since the temperatures in the two reactors can be chosen freely within wide ranges by corresponding fuel supply, it also is possible to employ different temperatures in the
25 two reactors - if expedient in other applications.

The invention will furthermore be described with reference to Fig. 1. All features illustrated and described per se or in any combination form the subject-matter of the invention.

In the drawing:

Fig. 1 shows a schematic representation of the process according to the invention.

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Via conduits 1 and 2 the solids are introduced into the first preheating stage 10 in the form of particles or pellets. In conduit 2, a mixture of fresh solids and hot off-gases from conduit 23 is obtained already. In the first preheating stage 10 the fresh solids from conduit 1 then are heated by the gas from conduit 23 and the off-gas is discharged via conduit 11.

Via conduit 12, the heated solids are supplied to a second preheating stage 13. Into this second preheating stage 13, conduit 22 opens and introduces hot gas into the second preheating stage 13 for preheating, wherein the gas then is withdrawn via conduit 23 and is again used as heat-transfer medium in the first preheating stage 10 in slightly cooled form.

The solids preheated further are withdrawn via conduit 14 and supplied to a third preheating stage 15. The same is fed with the heat-transfer medium from conduit 21, which subsequently is again discharged from the cyclone 15 via conduit 22. This interconnection in general leads to the fact that the individual preheating stages are flown through counter-currently, i.e. the solids are more and more heated via the individual preheating stages and off-gas cools down more and more. This results in a maximum heat transfer. Preferably, the preheating stages are designed as cyclones.

From the third preheating stage 15 the solids are withdrawn via conduit 16 and supplied to a solids conveyor 18, from where the solids get into the first reactor 20 via conduit 19. Said first reactor advantageously is designed as fluidized-bed reactor, particularly preferably as circulating fluidized bed.

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Via conduit 24, fuel, preferably in liquid or gaseous form, particularly preferably as methane-containing or hydrogen-containing gas, is introduced into the first reactor 20. Via conduit 25 the heated solids are withdrawn and supplied to a
5 further solids conveyor 26, from where they are supplied to the second reactor 30 via conduits 27, 28. Said second reactor may be of a stationary fluidized type or likewise preferably is be designed as circulating fluidized-bed reactor. Via conduit 31 it can also be supplied with fuel or hot gas. The gas is withdrawn via conduit 32 and supplied to a cyclone 33 or another gas-solids separator.

10 From the gas-solids separator 33, preferably a cyclone, a contaminated off-gas is withdrawn via conduit 34, while via conduit 35 the product is supplied to a solids conveyor 36. From the solids conveyor 36 parts of the solids are recirculated into the reactor via conduit 37 and conduit 28, in order to further improve
15 the product quality.

Via conduit 38 the other part of the product gets into the cooler 40. In said cooler, the product is cooled by means of air which is introduced into the cooler 40 and conduit 43 via conduit 41 and the condenser 42. The cooled product is
20 discharged via conduit 47.

The air heated as a result of cooling can be introduced into the first reactor 20 via conduits 44 and 45 and preferably be used there as fluidizing gas. It likewise is conceivable to introduce this air instead or also proportionately via conduit 46
25 into the second reactor 30.

List of Reference Numerals

	1, 2	conduit
5	10	preheating stage
	11, 12	conduit
	13	preheating stage
	14	conduit
	15	preheating stage
10	16	conduit
	17	solids conveyor
	18	conduit
	20	first reactor
	21-25	conduit
15	26	gas-solids conveyor
	27, 28	conduit
	30	second reactor
	31, 32	conduit
	33	gas-solids separator
20	34, 35	conduit
	36	solids conveyor
	37, 38	conduit
	40	cooler
	41	conduit
25	42	condenser
	43 - 47	conduit

Claims:

1. A process for the thermal treatment of contaminated solids, comprising the following steps:

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i) preheating of the contaminated solids in at least one preheating stage to a temperature between 100 and 600 °C by through-flow with a heat-transfer medium,

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ii) heating of the contaminated solids in a first reactor to a temperature between 600 and 1300 °C, whereby the impurities contained in the solids are at least partly driven out in gaseous form and an off-gas is obtained,

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iii) thermal treatment of the solids in a second reactor at a temperature between 600 and 1300 °C, whereby impurities contained in the solids are at least partly driven out in gaseous form and

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iv) routing of the off-gas into the at least one preheating stage as heat-transfer medium.

2. The process according to claim 1, **characterized in** that solids and heat-transfer medium are counter-currently guided through the at least one preheating stage.

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3. The process according to any of the preceding claims, **characterized in** that the first and/or the second reactor is operated in a reducing or oxidizing atmosphere.

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4. The process according to any of the preceding claims, **characterized in** that the energy input into the first and/or the second reactor is effected by supplying a fuel which is burnt in the first and/or the second reactor.

5 5. The process according to any of claims 1 to 4, **characterized in** that the energy input into the first and/or the second reactor is at least partly be effected by supplying a hot gas.

10 6. The process according to any of the preceding claims, **characterized in** that after process step (iv) the solids are at least partly cooled by a gas and that the gas heated thereby is introduced into the first and/or the second reactor.

15 7. The process according to any of the preceding claims, **characterized in** that the solids contain phosphate and/or cadmium content between 1 and 500 ppm.

20 8. The process according to any of the preceding claims, **characterized in** that the first and/or the second reactor is/are operated as fluidized-bed reactor with a stationary or a circulating fluidized bed.

9. The process according to claim 8, **characterized in** that spheres with a diameter of 0,05-50 mm are present in the fluidized-bed reactor.

25 10. An apparatus for the thermal treatment of contaminated solids, comprising at least one preheating stage (10, 13, 15) for preheating the solids to a temperature between 100 and 600 °C of the solids with a heat-transfer medium, a first reactor (20) for heating the solids to a temperature between 600 and 1300 °C, whereby impurities contained in the solids are at least partly in gaseous form and an off-gas is obtained and a second reactor (30) for the thermal treatment of the solids at a temperature between 600 and 1300 °C, whereby impuri-

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– 3 –

ties contained in the solids are driven out at least partly in gaseous form, characterized by at least one return conduit (21, 22, 23) from the first reactor (20) into at least one preheating stage (10, 13, 15) through which the off-gas is introduced into the at least one preheating stage (10, 13, 15) as a heat-transfer medium.

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11. The apparatus according to claim 10, **characterized in** that at least one preheating stage (10, 13, 15) is designed as cyclone.

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12. The apparatus according to claim 10 or 11, **characterized in** that the first reactor (20) and/or the second reactor (30) is/are designed as stationary or circulating fluidized bed reactor.

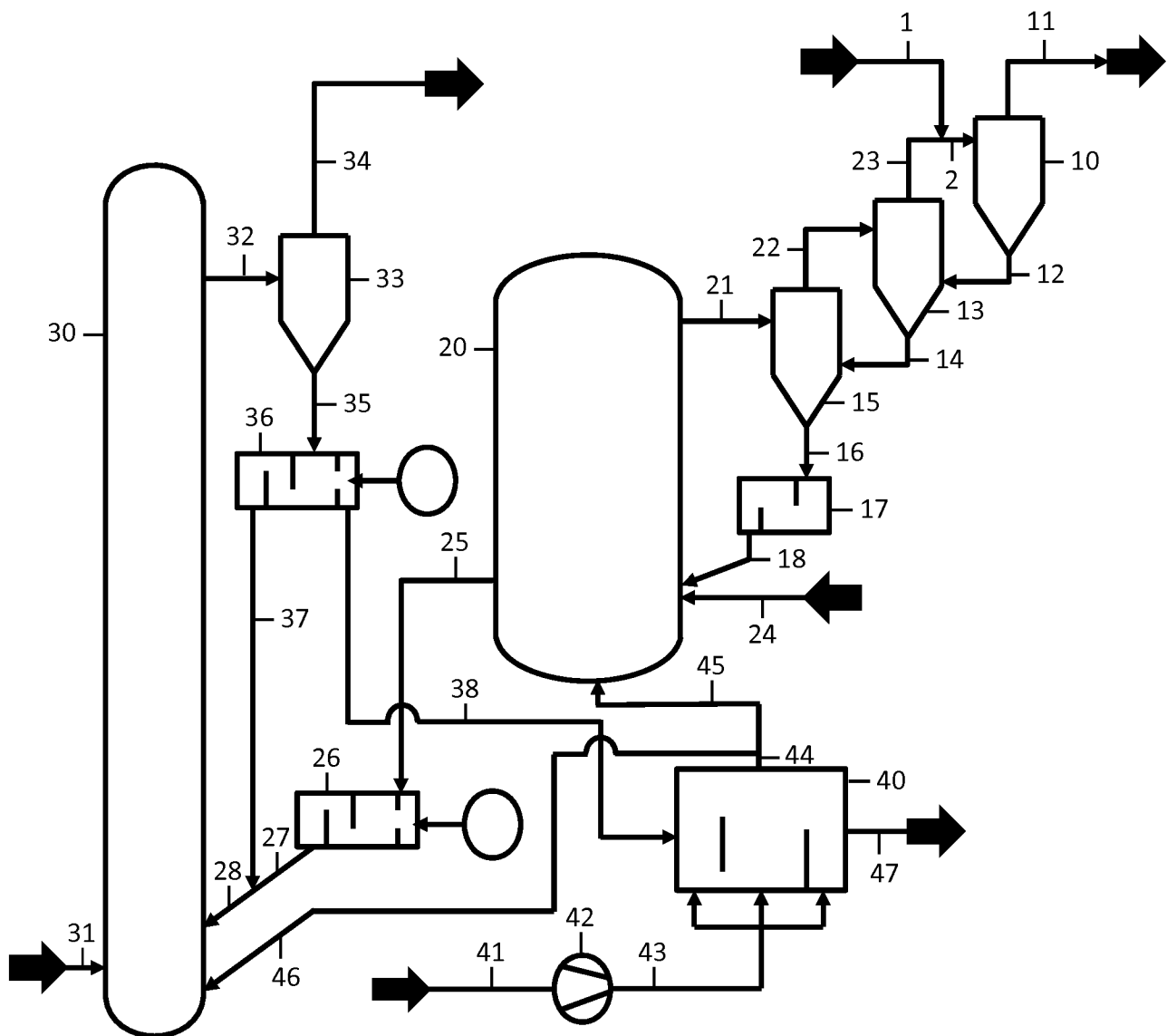


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J8/26 B01J8/34 B01J8/36 B01J6/00
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)
B01J

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

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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
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