

AUSTRALIA

PATENTS ACT 1990

SPRUSON & FERGUSON

65 1763

**PATENT REQUEST: STANDARD PATENT**

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

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**[54] Invention Title:**

A Process for the Separation of Catalyst-Free Working Solution  
From the Hydrogenation Circuit of the Anthraquinone Process for  
the Production of Hydrogen Peroxide

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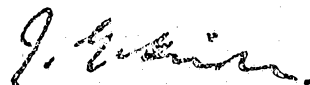
**[32] Application Date:**

25 May 1992

DATED this TWENTY FIRST day of MAY 1993

Degussa Aktiengesellschaft

By:



Registered Patent Attorney

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NOTICE OF ENTITLEMENT

I, John Gordon Hinde, of Spruson & Ferguson, St Martins Tower, 31 Market Street, Sydney, New South Wales 2000, Australia, being the patent attorney for the Applicant(s)/Nominated Person(s) in respect of an application entitled:

A Process for the Separation of Catalyst-Free Working Solution  
From the Hydrogenation Circuit of the Anthraquinone Process for  
the Production of Hydrogen Peroxide

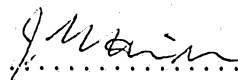
state the following:-

The Applicant(s)/Nominated Person(s) has/have entitlement from the actual inventor(s) as follows:-

The Applicant(s)/Nominated Person(s), by virtue of a Contract of Employment between the actual inventor(s) as employee(s) and the Applicant(s)/Nominated Person(s) as employer(s), is a person entitled to have the patent assigned to it if a patent were granted on an application made by the actual inventor(s).

The Applicant(s)/Nominated Person(s) is/are the applicant(s) of the basic application(s) listed on the Patent Request. The basic application(s) listed on the Patent Request is/are the application(s) first made in a Convention Country in respect of the invention.

DATED this 21st day of May 1993

  
John Gordon Hinde

IRN:

INSTR CODE:

<sup>3</sup>  
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(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. **651763**

- (54) Title  
**PROCESS FOR SEPARATION OF CATALYST-FREE WORKING SOLUTION FROM THE HYDROGENATION CIRCUIT OF THE ANTHRAQUINONE PROCESS FOR PRODUCTION OF HYDROGEN PEROXIDE**
- (51)<sup>5</sup> International Patent Classification(s)  
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- (56) Prior Art Documents  
**US 3433358  
GB 959583  
DE 1064949**
- (57) Claim

1. A process for the removal of catalyst-free working solution from working solution containing palladium black of the hydrogenation circuit of the anthraquinone process for the production of hydrogen peroxide using a microfiltration filter, the differential pressure between the retentate side and the permeate side being briefly reversed on a periodic basis, characterized in that a microfilter operated on the crossflow principle with a filter membrane of ceramic material or polyolefin having an average pore diameter of 0.1 to 3.0µm is used for the separation.

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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

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Invention Title:

A Process for the Separation of Catalyst-Free Working  
Solution From the Hydrogenation Circuit of the  
Anthraquinone Process for the Production of Hydrogen  
Peroxide

The following statement is a full description of this invention, including the  
best method of performing it known to me/us:-

A process for the separation of catalyst-free working solution from the hydrogenation circuit of the anthraquinone process for the production of hydrogen peroxide

#### Description

This invention relates to a process for the separation of catalyst-free working solution from working solution containing palladium black of the hydrogenation circuit of the anthraquinone process for the production of hydrogen peroxide.

In the anthraquinone process for the production of hydrogen peroxide, also known as the AO process, a reaction support based on one or more 2-alkyl anthraquinones and tetrahydro-2-alkyl anthraquinones is converted with hydrogen into the corresponding hydroquinone form in an organic solvent system in the presence of a catalyst. After the hydrogenation stage, the working solution freed from the catalyst is treated with an oxygen-containing gas in the oxidation stage, the quinone form of the reaction support reforming with elimination of hydrogen peroxide. Finally, hydrogen peroxide is extracted from the oxidized working solution with water and the working solution, i.e. the mixture of the reaction support and solvent or solvent mixture, is returned to the hydrogenation stage. Full particulars of the AO process can be found in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition (1989), Vol. A 13, pages 447-456.

Where suspension catalysts, such as palladium black for example, are used, the circuit of the hydrogenation stage (see, for example, US-PS 4,428,923) essentially comprises the actual reactor, a circulation pipe with a circulation pump, means for introducing and distributing the hydrogen, means for introducing working solution from the working solution drying stage follow-

ing the extraction stage and means for removing catalyst-free hydrogenated working solution, including a solid/liquid separator.

5 The quantitative and - in continuous operation - uninterrupted retention of the generally very finely divided suspension catalyst in the hydrogenation circuit during separation of part of the hydrogenated working solution, which is delivered to the oxidation stage, is a basic prerequisite for a safe and economic process.

10 Accordingly, numerous documents are concerned with this particular aspect, the solid/liquid separation being based on filtration using fine-pored filters and catalyst deposited on the filter surface being periodically removed therefrom either completely or in part by

15 pressure reversal and being delivered to the hydrogenation circuit (see, for example CA-PS 1,208,619, GB-PS 959,583 and US-PS 3,433,358).

According to CA-PS 1,208,619, suspended hydrogenation catalysts with a particle spectrum of 75% > 1  $\mu\text{m}$

20 can be separated from a working solution for the production of hydrogen peroxide using a filter medium of sintered steel particles having a maximum pore diameter of 8  $\mu\text{m}$ . Satisfactory operation of the filter on a continuous basis necessitates backwashing at frequent

25 intervals. Only suspension catalysts with the particle spectrum mentioned above can be separated. The process acknowledged above cannot be used for the separation of a catalyst-free working solution from a working solution containing a noble metal black, for example palladium

30 black having a primary particle spectrum of 5 to 50 nm (see Example 3).

A particular embodiment of the hydrogenation circuit of the anthraquinone process for the production of hydrogen peroxide is disclosed in GB-PS 959,583.

35 Part of the hydrogenated working solution is removed in

catalyst-free form from the circulated working solution containing palladium catalyst by means of a filter in a filter housing through which the catalyst-containing working solution flows. The filter is periodically  
5 backwashed to free the surface of the filter at least from partly deposited catalyst. No particulars of the filter medium are provided in this document. A major disadvantage of this process is that the volume of catalyst-containing working solution present in the  
10 filter housing(s), based on the volume present in the hydrogenation circuit as a whole, is very considerable. Accordingly, this embodiment involves an undesirably high tie-up of capital.

Effective filter media for separating support-free noble metal catalysts, such as palladium black, are known from US-PS 3,433,358. The filter media in ques-  
15 tion are filter candles of carbon material of which the pore diameter may be larger than the diameter of the particles to be separated and which have a wall thick-  
20 ness of at least 10 mm. In this case, too, one or more filter candles are arranged in a correspondingly shaped filter housing. Although this document seeks to mini-  
mize the volume in the filter housings in order to reduce the capital tied up in the catalyst-containing  
25 working solution remaining in this unit, narrow limits are imposed by the design of the filter candles to maintain a certain filter area and have already been reached in practice. Filter candles of the type men-  
tioned above, which are periodically backwashed in  
30 operation, are used in the industrial production of hydrogen peroxide, for example by the process according to US-PS 4,428,923.

In the search to improve the production of hydrogen peroxide by the anthraquinone process in order  
35 to reduce costs, there is considerable interest in

modifying the apparatus for separating a catalyst-free working solution from the hydrogenation circuit in such a way that the volume of working solution remaining in the solid/liquid separator and the quantity of catalyst present therein can be significantly reduced for the same filtration capacity.

DE-OS 32 45 318 describes a process for continuously carrying out gas/liquid pressure reactions using a suspended catalyst remaining in the reaction zone, in which part of the reaction liquid is removed from the reaction vessel using a microfilter operated on the crossflow principle. The microfilters are equipped with a tube, hose or plate module, polytetrafluoroethylene, polyvinylidene fluoride and sintered metals being mentioned as suitable materials for the module. The microfilter is periodically backwashed by pressure reversal between the retentate side and the permeate side of the microfilter. References to the production of hydrogen peroxide by the anthraquinone process using extremely fine noble metal blacks are as difficult to find in this document as references to the solution to the problem addressed by the invention as stated above. Thus, the catalyst used by way of example in the process according to DE-OS 32 45 318 has an average particle size of around 1  $\mu\text{m}$  whereas the primary particles of palladium black are between 5 and 50 nm in size. DE-OS 30 40 631 is based on a process principle similar to DE-OS 32 45 318: among the catalysts mentioned by way of example, there is again no reference to the particularly fine-particle noble metal blacks.

The present invention relates to a process for the removal of catalyst-free working solution from working solution containing palladium black of the hydrogenation circuit of the anthraquinone process for the production of hydrogen peroxide using a microfiltra-

tion filter, the differential pressure between the retentate side and the permeate side being briefly reversed on a periodic basis, characterized in that a microfilter operated on the crossflow principle with a filter membrane of ceramic material or polyolefin having an average pore diameter of 0.1 to 3.0  $\mu\text{m}$  is used for the separation.

It was not foreseeable that a completely catalyst-free working solution would be able to be removed from the hydrogenated working solution containing palladium black by means of a crossflow microfilter with the claimed filter membrane, even in continuous operation. The stated problem cannot be solved satisfactorily, if at all, using other filter materials: sintered metal filters of stainless steel with a pore diameter of 1.4  $\mu\text{m}$  are neither sufficiently impervious to noble metal blacks, nor can they be satisfactorily backwashed (see Example 3). In addition, in the sintered metal filter mentioned, so-called blockage of the pores soon occurs with an unacceptable reduction in the permeate flux. However, counteracting the unacceptable, rapid reduction in the permeate flux necessitates frequent stoppages to enable the membrane filters to be chemically cleaned.

Although a filter membrane of other organic polymers than polyolefins, more particularly polypropylene, for example fluorine-containing polymers, may have the necessary impermeability to noble metal blacks in individual cases, their mechanical stability is unsatisfactory and/or material failures occur at the welds and bonds between the filter membrane and other plastic parts of the housing, resulting in stoppages.

Whereas the maximum permitted differential pressure between the permeate side and the retentate side has to be limited to around 200 kPa in the case of

a polypropylene membrane, microfilters with a filter membrane of a ceramic material can even be operated at much higher differential pressures. This is a major advantage of the microfilters equipped with a ceramic membrane because the specific permeate flux increases with increasing transmembranal differential pressure. Accordingly, it is possible by increasing the transmembranal differential pressure to reduce the necessary filter area or the number of filters and hence the investment volume for the same filtration efficiency.

The filter membrane best consists of an oxidic ceramic material which is chemically inert to the working solution and which does not adsorb any constituents of the working solution, preferably an oxidic ceramic material of essentially  $\alpha$ -aluminium oxide, the pore diameter best being between 0.1 and 1.0  $\mu\text{m}$  and, more particularly, between 0.1 and 0.5  $\mu\text{m}$ .

The construction principle of a microfilter with a filter membrane is known per se. One or more tube or hose, plate or wound modules each containing the effective filter membrane is/are arranged in a filter housing. The membrane layer is situated on a coarse-pored support layer of the same material or a different material. The filter modules are arranged in the housing in such a way that they separate the retentate side from the permeate side. So-called tube modules, particularly in the form of multichannel elements, are suitable for the process according to the invention. The multichannel elements are elongate cylindrical elements with several round or elliptical longitudinal channels. The element itself consists of a porous material, preferably an oxide ceramic, more particularly one based on  $\alpha$ -aluminium oxide. The actual filter membrane is situated on the wall of the channels. The channels are typically between 1 and 10 mm in diameter.

Multichannel elements with a channel diameter of 2 to 6 mm are particularly suitable for the process according to the invention. By virtue of the construction, a large filter area is thus concentrated in a confined space. It is possible in this way to accommodate a large filter area and hence a large filter capacity in a confined space. This is an advantage of considerable importance in the claimed process because investment volume and the space required in a plant can be considerably reduced in this way.

As mentioned above, filter candles are used in the known process. To achieve the necessary stability and filter capacity, these filter candles are several times larger in their internal diameter. Accordingly, by comparison with the filter unit according to the invention, known filter candles necessitate much larger filter housings. At the same time, the channel volume of the filter elements according to the invention, through which the palladium-containing working solution flows, is considerably smaller than the corresponding volume in the filter housing for the filter candles. Accordingly, changing from the known filter candles to the filter elements according to the invention also provides for a distinct reduction in the holdup of working solution and palladium (see Example 4).

The flow rate of the palladium-containing working solution transversely of the filtration direction is generally adjusted to values of 0.5 to 5 m/s, a flow rate of 1 to 2 m/s being preferred. By virtue of these unexpectedly low flow rates, the pressure loss and hence the specific energy demand of the process according to the invention are minimal. The pressure of the hydrogenation circuit prevails on the retentate side during the filtration process; the pressure difference towards the permeate side will be greater than zero and hence

lower than the pressure on the retentate side. In the process according to the invention, the transmembranal differential pressure is preferably greater than 200 and smaller than 500 kPa. Using the preferred filter elements with a membrane of  $\alpha$ -aluminium oxide, the specific permeate flux increases linearly over a wide range with increasing transmembranal pressure difference (see Example 1).

For backwashing, the pressure between the retentate side and the permeate side is reversed to maintain a constant high mean value of the permeate flow. Microfilters with a filter membrane according to the invention can be effectively backwashed and are distinguished by high specific fluxes in an average cycle. Surprisingly - and this is another advantage of the process according to the invention - the specific permeate flux ( $\text{m}^3/\text{h}$  and  $\text{m}^2$ ) is considerably greater than in the case of filtration using known filter candles. It is thus possible to reduce the installed filter area in the process according to the invention in relation to the known process. Another advantage of the process according to the invention is that, even after long periods of operation, no catalyst deposits occur either in the filter housings or in the filter elements.

The measures according to the invention for separating a catalyst-free working solution from a hydrogenated working solution containing suspension catalysts can be implemented very effectively in all known AO processes using palladium black. Information on how the hydrogenation stage is carried out and on suitable apparatus can be found in US-PS 4,428,923 and US-PS 3,423,176 cited therein and in DE-OS 40 29 784. The invention is illustrated by the following Examples and Comparison Examples.

### Examples 1 to 3

Determination of the effectiveness of various filter modules for the separation of catalyst-free working solution from working solution containing Pd black:

5           In a pilot-plant apparatus, palladium-containing working solution was circulated by a pump through the filtration module operated on the crossflow principle via a tank B1. The permeate entering the shell space of the module through the filter medium is also returned to  
10 the tank B1 via a tank B2 and a safety filter. Backwashing takes place from the tank B2. A working solution essentially based on an aromatic hydrocarbon boiling at 185 to 205°C and tetrabutyl urea as solvent and a mixture of 2-ethyl anthraquinone and 2-ethyl  
15 tetrahydroanthraquinones as reaction support was used for the tests. The Pd content in the circuit was adjusted to approximately 2 g/l.

### Example 1

20           Commercially available multichannel ceramic filter elements with an internal channel diameter of approximately 3 mm were used in the apparatus described above: filter membrane of essentially  $\alpha$ -aluminium oxide (99.95%); mean pore diameter approx. 0.2  $\mu\text{m}$ ; pore volume  
25 30%; thickness of membrane 8 to 12  $\mu\text{m}$ ; filter area 0.44  $\text{m}^2$ . Support material (support)  $\alpha$ -aluminium oxide, pore diameter 7 to 11  $\mu\text{m}$ , pore volume approx. 30%.

          As can be seen from Table 1 below, the specific permeate flux increases with increasing mean transmembranal pressure difference (as measured immediately  
30 after backwashing). The influence of the crossflow rate is minimal up to a transmembranal differential pressure of approximately 400 kPa.

Table 1

Mean trans-membranal pressure difference kPa	Specific permeate flux (l/m <sup>2</sup> h)	
	Crossflow 1.5 m <sup>3</sup> /h	Crossflow 3 m <sup>3</sup> /h
40		180
100	580	580
140	820	
170		1140
250	1540	
270		1700
350		2380
360	2340	
425	2560	
500		3220
570	2980	3430

The module is impermeable to palladium black. Backwashing is necessary to maintain a constant average permeate flux. A backwashing time of 10 seconds for a filtration time of 10 minutes is sufficient to maintain the desired mean permeate flux over prolonged operating times.

#### Example 2

A filter module with 43 filter tubes with a filter membrane of polypropylene in a support tube of stainless steel was used; membrane pore diameter 0.2  $\mu\text{m}$ ; filter area 1 m<sup>2</sup>; crossflow rate 1 m/s.

The membrane was impermeable to palladium black and could be effectively backwashed. In the permitted

range (to max. 200 kPa) the permeate flux increases linearly and substantially independently of the cross-flow rate, amounting to 750 l/m<sup>2</sup>h for a transmembranal pressure difference of 150 kPa.

### Example 3 (Comparison)

5           A sintered metal filter of stainless steel with  
a pore diameter of 1.4  $\mu$ m was used; filter area 0.1 m<sup>2</sup>.  
Permeate flux was studied as a function of the filtra-  
tion time using the following cycle times: filtration  
300 s, expansion 1.5 s, backwashing 15 s, circulation  
10 volume 6.5 m<sup>3</sup>/h. Pressure before the filter 400 kPa,  
after the filter 100 kPa.

15           The filter was not impermeable to palladium  
black. In addition, permeate flux falls by more than  
50% of the initial value in the first 12 cycles.  
Accordingly, the blockage of the filter element cannot  
be eliminated by backwashing.

### Example 4

20           In a plant for the production of hydrogen perox-  
ide by the AO process, filter candles are installed in  
a filter housing according to US-PS 3,433,358 to sepa-  
rate working solution free from Pd black from the  
hydrogenation circuit according to US-PS 4,428,923. The  
replacement of this filter unit by a filter unit accord-  
25 ing to the invention comprising filter elements accord-  
ing to Example 1 affords major advantages for the same  
forward flow (= permeate volume/h), as listed in the  
following in relation to the values of the prior art:

30   Specific permeate flux:   increased by a factor of 1.6  
Filter area:                reduced by approx. 40%  
Volume of working solution  
in the total number of  
filter housings required: reduced by 89%

5 Total amount of palladium  
remaining in the filter  
unit (in the suspension  
and on the filter  
surface): reduced by 93%

#### Example 5

10 In a production plant for the production of  
hydrogen peroxide, the process according to the inven-  
tion was carried out in the bypass for 4 weeks under the  
following conditions:

15	Membrane area:	3.1 m <sup>2</sup>
	Membrane material:	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , pore diameter approx 0.2 $\mu$ m
	Filtrate capacity:	5.9 m <sup>3</sup> /h
	Transmembranal pressure difference:	240 kPa
	Crossflow rate	1.85 m/s
20	Filtration time to backwashing time:	300 s/10 s

25 No malfunctions occurred. In the subsequent  
inspection, no catalyst deposits were found either in  
the filter housing or in the filter elements.

The claims defining the invention are as follows:

1. A process for the removal of catalyst-free working solution from working solution containing palladium black of the hydrogenation circuit of the anthraquinone process for the production of hydrogen peroxide using a microfiltration filter, the differential pressure between the retentate side and the permeate side being briefly reversed on a periodic basis, characterized in that a microfilter operated on the crossflow principle with a filter membrane of ceramic material or polyolefin having an average pore diameter of 0.1 to 3.0 $\mu$ m is used for the separation.
2. A process as claimed in claim 1, characterized in that the membrane consists of essentially  $\alpha$ -aluminium oxide and the mean pore diameter is in the range from 0.1 to 1.0 $\mu$ m and, more particularly, in the range from 0.1 to 0.5 $\mu$ m.
3. A process as claimed in claim 1 or 2, characterized in that the flow rate transversely of the filtration direction is between 0.5 and 5m/sec.
4. A process for the removal of catalyst-free working solution from working solution containing palladium black of the hydrogenation circuit of the anthraquinone process for the production of hydrogen peroxide using a microfiltration filter substantially as hereinbefore described with reference to any one of the Examples but excluding the comparative examples.

**Dated 20 May, 1993**  
**Degussa Aktiengesellschaft**

**Patent Attorneys for the Applicant/Nominated Person**  
**SPRUSON & FERGUSON**

A process for the separation of catalyst-free working solution from the hydrogenation circuit of the anthraquinone process for the production of hydrogen peroxide

#### Abstract

The invention relates to a process for the separation of catalyst-free working solution from working solution containing palladium black of the hydrogenation circuit of the anthraquinone process for the production of hydrogen peroxide.

The problem addressed by the invention was to improve the separation of a catalyst-free working solution from the hydrogenation circuit containing Pd black, which was previously carried out using filter candles, in order to reduce the process costs.

This problem is solved by the use of a micro-filter operating on the crossflow principle with a filter membrane of ceramic material, more particularly  $\alpha$ -aluminium oxide, or polyolefin with an average pore diameter of 0.1 to 3.0  $\mu\text{m}$ . The crossflow rate is generally 0.5 to 5 m/sec.