

COMMONWEALTH OF AUSTRALIA

610675

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address (es).

Kx ⁽¹⁾ HOECHST AKTIENGESELLSCHAFT,
We of 45 Bruningstrasse, D-6230 Frankfurt/Main,
Federal Republic of Germany.

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: ⁽²⁾
PROCESS FOR THE RECOVERY OF RHODIUM FROM AQUEOUS
SOLUTIONS CONTAINING RHODIUM COMPLEX COMPOUNDS.

(3) Here insert number(s) of basic application(s)

which is described in the accompanying complete specification. This application is a
Convention application and is based on the application numbered ⁽³⁾

P 37 44 213.9

(4) Here insert Name of basic Country or Countries, and basic date or dates

for a patent or similar protection made in ⁽⁴⁾ Federal Republic of
Germany on 24th December, 1987.

My
Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys,
50 Queen Street, Melbourne, Victoria, Australia.

DATED this 22nd day of December, 1988

(5) Signature (s) of Applicant (s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

(5)

HOECHST AKTIENGESELLSCHAFT

By: 

IAN A. SCOTT

Registered Patent Attorney

23/12/88

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Patents Act 1952-1969

DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION(1) Here
insert (in
full) Name of
Company.In support of the Convention Application made by⁽¹⁾.....
HOECHST AKTIENGESELLSCHAFT(2) Here
insert title
of Invention.(hereinafter referred to as the applicant) for a Patent
for an invention entitled:⁽²⁾.....
PROCESS FOR THE RECOVERY OF RHODIUM FROM AQUEOUS
SOLUTIONS CONTAINING RHODIUM COMPLEX COMPOUNDS(3) Here
insert full Name
and Address,
of Company
official
authorized
to make
declaration.I, ⁽³⁾.....KARL-FINZ REICHEL, ..
of.....4200 Oberhausen, Federal Republic of Germany.

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent
to make this declaration on its behalf.(4) Here
insert basic
Country or
Countries
followed by
date or dates
and basic
Applicant or
Applicants.2. The basic application as defined by Section 141 of the Act was
made in⁽⁴⁾.....Federal Republic of Germany
on the.....24th.....day of.....December 1987, by.....
RUHRCHEMIE AKTIENGESELLSCHAFT

XX

(5) Here
insert (in
full) Name
and Address
of Actual
Inventor or
Inventors.3.⁽⁵⁾.....Dr. Gerhard Diekhaus, Walsumermarkstr. 89,
Oberhausen 11, Harald Kappesser, Waidmannsweg 24,
Oberhausen 11, Federal Republic of GermanyXX/are the actual inventors of the invention and the facts upon which the applicant
is entitled to make the application are as follow:The applicant is the assignee of.....RUHRCHEMIE AKTIENGESELLSCHAFT
who in turn is the assignee of the said actual inventor:4. The basic application referred to in paragraph 2 of this Declaration
was.....the first application made in a Convention country in
respect of the invention the subject of the application.DECLARED at.....Oberhausen 11
this.....28th.....day of.....November,.....19 88

(12) PATENT ABRIDGMENT (11) Document No. AU-B-27500/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No 610675

(54) Title
PROCESS FOR THE RECOVERY OF RHODIUM FROM AQUEOUS SOLUTIONS
CONTAINING RHODIUM COMPLEX COMPOUNDS

International Patent Classification(s)
(51)⁴ C01G 055/00 B01J 031/20

(21) Application No. : 27500/88 (22) Application Date : 23.12.88

(30) Priority Data

(31) Number (32) Date (33) Country
3744213 24.12.87 DE FEDERAL REPUBLIC OF GERMANY

(43) Publication Date : 29.06.89

(44) Publication Date of Accepted Application : 23.05.91

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(56) Prior Art Documents
AU 76590/87 C07C 51/41 C01G 55/00
US 4346570
US 4341741

(57) Claim

1. A process for the recovery of rhodium from aqueous solutions containing rhodium complex compounds, characterised in that these solutions are treated in a first stage at 80 to 140°C with oxygen or an oxygen-containing gas in the presence of a water-soluble salt of a carboxylic acid having 7 to 22 carbon atoms, and in a second stage at 50 to 140°C with hypochlorite.

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PATENTS ACT 1952-69

610675 Form 40

COMPLETE SPECIFICATION

(ORIGINAL)

Class

Int. Class

Application Number:
Lodged:

Complete Specification Lodged:

Accepted:

Published:

Priority:

Related Art

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Complete Specification for the invention entitled:

PROCESS FOR THE RECOVERY OF RHODIUM FROM AQUEOUS
SOLUTIONS CONTAINING RHODIUM COMPLEX COMPOUNDS.

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

US

Process for the recovery of rhodium from aqueous solutions containing rhodium complex compounds

The present invention relates to a process for the recovery of rhodium from rhodium complex compounds which have been used as catalysts in the form of aqueous solutions.

Rhodium complex compounds are being increasingly used as catalysts or catalyst constituents in industrial processes for the production of organic chemicals.

Thus the DE-C1-26 27 354 describes a hydroformylation process which is characterised by the use of catalytically active rhodium complex compounds which contain water-soluble sulfonated arylphosphines as ligands.

The cost-effectiveness of such processes greatly depends on the rhodium being recovered from the inactive catalysts without any appreciable loss. When the catalysts are used over a prolonged period, their activity and selective action diminishes. This reduction in performance is caused by various factors. In the course of time contaminants in the reactants lead to irreversible poisoning of the catalysts. Chemical transformations of the complex ligands under the reaction conditions or reactions of the complex compounds with the reaction products can lead to a partial or

complete loss of catalytic activity. Therefore, the catalysts have to be regenerated from time to time. All that is generally done is to recover the rhodium and transform it again into the compound used as a catalyst.

A process described in the German patent application P 36 26 536.5 has proved highly successful for the recovery of rhodium from aqueous solutions containing rhodium complex compounds. It consists in the fact that the water-soluble salt of a carboxylic acid having 7 to 22 carbon atoms is added to the solution containing a rhodium complex compound in excess, related to the rhodium, the solution is then treated with an oxidant, in particular oxygen or air, at 50 to 200°C and the rhodium precipitated as a water-insoluble compound is separated. With this method 90% and more of the rhodium originally contained in the solution is recovered in commercial operations.

The remaining amounts of rhodium can only be separated by complicated means, e.g. by oxidation at high temperature and high pressure or by thermal decomposition, optionally in the presence of a carrier material onto which the rhodium can precipitate. However, when high temperatures are used, there is a danger of the rhodium occurring in a metallic form or in the form of compounds which cannot be directly converted into the

active hydroformylation catalyst.

Another method of separating rhodium is the use of high-grade oxidants, such as hydrogen peroxide. However, their use on a commercial scale has its limits. Arguments against them are economic considerations as well as difficulties in handling the oxidants and environmental problems involved in their use.

The task of the present invention is to eliminate the shortcomings described above and to separate the major part of the rhodium from the aqueous solution by simple means. The noble metal is to occur in a form which guarantees its trouble-free reuse as a hydroformylation catalyst.

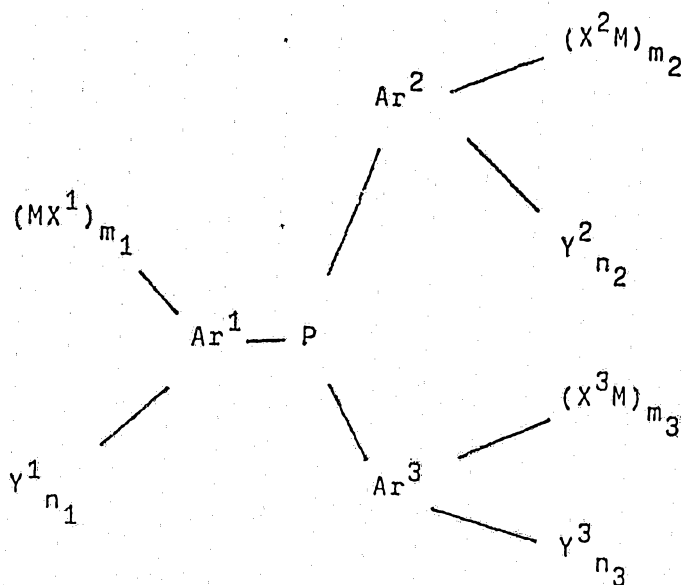
The invention consists in a process for the recovery of rhodium from aqueous solutions containing rhodium complex compounds. It is characterised in that these solutions are treated in a first stage at 80 to 140°C with oxygen or an oxygen-containing gas in the presence of a water-soluble salt of a carboxylic acid having 7 to 22 carbon atoms, and in a second stage at 50 to 140°C with hypochlorite.

Surprisingly, the task described above is solved by the new process. The claimed procedure not only ensures

that rhodium is recovered in high yields but also that it can be transformed directly into the active hydroformylation catalyst, i.e. e.g. by simple treatment with carbon monoxide and hydrogen, optionally in the presence of complexing agents. Furthermore, it is remarkable that overall the treatment times are short, which improves the cost-effectiveness of the process. Finally, no substances occur during the process which have to be treated specially to avoid a negative impact on the environment.

The aqueous solutions to be treated according to the new process can contain between 10 and 2000 weight ppm of rhodium in the form of a complex compound.

Preferably these are rhodium complex compounds which conform to the general formula $\text{HRh}(\text{CO})_x \text{L}_{4-x}$, x being the numbers 1 to 3. L denotes water-soluble ligands, in particular phosphines of the general formula



Here, Ar^1 , Ar^2 and Ar^3 each denote a phenyl or a naphthyl group, Y^1 , Y^2 and Y^3 each a straight-chain or branched alkyl group having 1 to 4 carbon atoms, an alkoxy group, a halogen atom, an OH, CN, NO_2 or $\text{R}^1\text{R}^2\text{N}$ group, where R^1 and R^2 are each a straight-chain or branched alkyl group having 1 to 4 carbon atoms; X^1 , X^2 and X^3 each denote a carboxylate- (COO^-) and/or sulfonate- (SO_3^-) group, n_1 , n_2 and n_3 are the same or different integers from 0 to 5. M stands for an alkali metal ion, the equivalent of an alkaline earth metal ion or zinc ion or an ammonium ion or quaternary alkyl ammonium ion of the general formula $\text{N}(\text{R}^3\text{R}^4\text{R}^5\text{R}^6)^+$, where R^3 , R^4 , R^5 and R^6 are each a straight-chain or branched alkyl group having 1 to 20 carbon atoms, and preferably R^3 is a straight-chain or branched alkyl group having 7 to 18 carbon atoms, and R^4 , R^5 and R^6 are straight-chain or branched alkyl groups having 1 to 4 carbon atoms; m_1 , m_2 and m_3 are the same or different integers from 0 to 3, at least one number m_1 , m_2 or m_3 being the same or greater than 1.

Apart from the rhodium complex compound the aqueous solution can contain free excess ligands as well as their conversion and degradation products. Finally, organic constituents, namely starting materials and products of the reaction which was catalysed by the rhodium complex compound, can be dissolved in the

compound depending on their solubility in water as well as other substances which were used to perform the reaction, such as amphiphilic reagents.

5 According to the invention the solution of the complex compound is initially treated with oxygen or an oxygen-containing gas, e.g. air, in the presence of a water-soluble salt of a carboxylic acid at 80 to 140°C. Optionally the reaction takes place at pressures of 0.1 to 2.0 MPa, preferably 0.2 to 1.0 and in particular 0.3 to 0.7 MPa.

10 It is preferable that the total concentration of the saline compounds in the solution to be worked up according to the new process is not to exceed 15% by weight. It is appropriate to keep to concentrations of 3 to 12, preferably 5 to 10% by weight of salt, related to the solution. If necessary, the salt concentration of the solution is to be adjusted to the above-mentioned values by adding water.

20 200 to 500, in particular 40 to 300 and preferably 50 to 200 moles of carboxylic acid salt are added to the aqueous solution per gramme-atom of rhodium.

25 The expression "saline compounds" used herein encompasses all salts which are contained in the solution. Free ligands and their "saline" transformation products and catabolic products are also included in the terms.

30 The carboxylic acid salts are derived from carboxylic acids having 7 to 22 carbon atoms. Salts of aliphatic, cycloaliphatic, aromatic and/or araliphatic carboxylic acids having 8 to 13 carbon atoms are given preference.



Of them the monocarboxylic acids are particularly suitable. Above all salts of branched aliphatic monocarboxylic acids, in particular salts of 2-ethylhexanoic acid, isononanoic acid and isotridecanoic acid, have proved particularly valuable. The terms isononanoic acid and isotridecanoic acid are understood to be the reaction products of diisobutylene or tetrapropylene obtained by hydroformylation and subsequent oxidation.

It is appropriate to pass the oxygen or the oxygen-containing gas through the heated solution via distributing facilities and optionally with stirring. It has proved successful to maintain a pH value of 4 to 8, preferably 5 to 7.5 and in particular 5.5 to 7 in the solution. The duration of the treatment depends particularly on the selected temperature and the oxygen supply. Reaction periods of 1 to 3 hours are generally sufficient.

After oxidation with oxygen or the oxygen-containing gas has been completed, rhodium separation is completed in a second reaction stage by the addition of hypochlorite.

It is not necessary to remove the previously precipitated water-insoluble rhodium compounds from the solution. The hypochlorite can be added to the solution

in the same reactor immediately after completion of the oxygen feed and adjustment to the required reaction temperature.

The hypochlorites preferred are the compounds soluble in water; the salts of calcium, sodium and potassium available on a commercial scale are used in particular.

Although it is possible to add the hypochlorite to the complex salt solution in substance, it is appropriate to use it dissolved in water. The concentration of this aqueous solution is not critical and can be varied within a wide range. It must only be ensured that the reaction solution is not excessively diluted.

The reaction with hypochlorite takes place at 50 to 140, in particular 70 to 120°C, advantageously with stirring. The reaction time depends on the temperature, but is shorter than in the first reaction stage. It is about 0.25 to 1.5 hours.

In order to achieve an optimum action of the hypochlorites, ^{preferably} pH values of between 3 and 6 and in particular of between 4 and 5 are maintained in the reaction solution.

The oxidants used in the two reaction stages, oxygen



and hypochlorite, are used in great excess, related to the rhodium. ^{Preferably} 2 to 20 m³ of oxygen/hour and 150 to 350 moles of hypochlorite are used per gramme-atom of rhodium. In this context it must be remembered that the amount of rhodium present in the solution is small and therefore the total amount of chemicals used is small.

The rhodium compounds formed by oxidation are insoluble in water and precipitate as an oily layer on the aqueous solution. The two phases are separated in a simple manner owing to their different densities. However, it is appropriate to take up the rhodium compounds in a water-insoluble organic solvent. This solvent is added to the reaction mixture at the beginning of or during the reaction. However, it is preferable to add it after the reaction has been completed. Suitable organic solvents are aliphatic hydrocarbons such as cyclohexane, aromatic hydrocarbons such as benzene, toluene or xylene, aliphatic carboxylic acids having 5 to 10 carbon atoms or their esters, aliphatic or cycloaliphatic ketones having 5 to 10 carbon atoms. Toluene is given preference.



The extraction of the rhodium compound with the organic solvent takes place at temperatures of between 10 and 100°C, preferably 40 to 60°C. If necessary, extraction can be repeated several times.

The solution of the rhodium compound in the organic solvent can be used directly again as a catalyst component. Naturally, it is also possible to transform it into a rhodium carbonyl compound by treatment with carbon monoxide and hydrogen or to convert it with the aqueous solution of the phosphorus ligand into a water-soluble rhodium complex compound.

The new process permits up to 95% of the original amount of rhodium to be separated from the aqueous solution in economically viable reaction periods.

The invention is described in greater detail in the following examples. However, it is not intended to limit it to these particular embodiments.

The examples 1 to 3 describe the treatment of an aqueous solution containing rhodium complex compounds with oxygen (in the form of air) alone and example 4 with sodium hypochlorite alone. Examples 5 to 13 relate to the two-stage oxidation according to the claimed process.

Examples 1 to 3

The amounts given in table 1 of 2-ethyl hexanoic acid and sodium-2-ethyl hexanoate are added in each case to 1000 g of an aqueous solution containing 93 weight ppm of rhodium in the form of a complex compound with tri-sodium-triphenylphosphine trisulfonate as a complex ligand and a total of 8.75 % by weight of salts. Over a period of 3 to 6 hours and at a pressure of about 0.2 MPa air is passed through the solution which has been heated to 100 to 120°C. A water-insoluble rhodium compound forms which is separated by extracting with toluene twice. The residual rhodium content is determined in the remaining water phase. The reaction conditions and results of the tests are summarised in table 1.

Example 4

1000 g of the solution employed in the examples 1 to 3 are used. After adjustment of the pH value in the solution by the addition of hydrochloric acid, the solution is heated to the reaction temperature and sodium hypochlorite is added with stirring as an aqueous solution with a content of 13 % by weight of hypochlorite (related to the solution). The solution is left to after-react, cool and is extracted with toluene as in the examples 1 to 3. The reaction conditions and

results of the test are compiled in table 2.

Examples 5 to 13

1000 g of the solution employed in examples 1 to 4 are used in each case. The samples are initially treated under identical conditions with air. Then the solution is reacted with sodium hypochlorite without prior separation of the precipitated rhodium compound. The reaction conditions and results of the tests are compiled in tables 3a and 3b.

Table 1

Example	Na-2-ethyl hexanoate (mol/g-at Rh)	2-ethyl hexanoic acid (mol/g-at Rh)	pH value	Temperature (°C)	Pressure (MPa)	Air (m ³ /h . g-at Rh)	Time (min)	Rh in aqueous solution (weight ppm)
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1	150	20	6.19	100	0.2	14	180	12.9
2	150	20	6.50	120	0.2	14	360	5.0
3	150	20	6.50	100	0.2	14	360	5.7

Table 2

Example	pH value	Temperature (°C)	NaOCl (mol/g-at Rh)	Time* (min)	Rh in aqueous solution (weight ppm)
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4	5.0	100	645	10+15	13
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* reaction and after-reaction time

Table 3a - treatment with air

- 15 -

0 1 2 3 4 5 6 7 8 9

Example 3b - treatment with NaOCl

Example	pH value	Temperature (°C)	NaOCl (mol/g-at Rh)	Time (min)	Rh in aqueous solution (weight ppm)
5	4.5	100	215	10+15	4.9
6	5.0	100	215	10+15	4.6
7	6.6	100	215	10+15	6.5
8	3.9	100	215	10+15	7.2
9	1.0	100	215	10+15	10.5
10	4.5	50	215	10+15	9.5
11	5.0	20	215	10+15	8.8
12	4.5	20	215	1440	8.1
13	4.5	100	22	10+15	8.5

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the recovery of rhodium from aqueous solutions containing rhodium complex compounds, characterised in that these solutions are treated in a first stage at 80 to 140°C with oxygen or an oxygen-containing gas in the presence of a water-soluble salt of a carboxylic acid having 7 to 22 carbon atoms, and in a second stage at 50 to 140°C with hypochlorite.
2. A process according to claim 1, characterised in that the treatment with oxygen or an oxygen-containing gas takes place at pressures of 0.1 to 2.0 MPa.
3. Process of claim 1 or claim 2 wherein the treatment with oxygen or an oxygen-containing gas takes place at 0.2 to 1.0 MPa.
4. Process of any one of claims 1 to 3 wherein the treatment with oxygen or an oxygen containing gas takes place at 0.3 to 0.7 MPa.
5. A process according to one or more of the claims 1 to 4, characterised in that the treatment with hypochlorite takes place at 70 to 120°.
6. A process according to one or more of the claims 1 to 5, characterised in that a pH value of between 3 and 6, in particular 4 and 5 is maintained in the solution to be treated with hypochlorite.



7. A process according to one or more of the claims 1 to 6, characterised in that 2 to 20 m³ of oxygen per hour and 150 to 350 moles of hypochlorite are used per gramme-atom of rhodium.

8. A process according to one or more of the claims 1 to 7, characterised in that the precipitated water-insoluble rhodium compound is extracted with toluene.

DATED this 20th day of February, 1991.

HOECHST AKTIENGESSELLSCHAFT

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TRADE MARK ATTORNEYS
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