4/

(CONVENTION. By one or more persons and/or a Company.) Form 4.

COMMONWEALTH OF AUSTRALIA **621968**

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).

~~I~~ We (1) HOECHST AKTIENGESELLSCHAFT
of 50 Bruningstrasse, D-6230 Frankfurt/Main 80, 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 SEPARATING ORGANOMETALLIC COMPOUNDS AND/OR METAL CARBONYLS FROM THEIR SOLUTIONS IN ORGANIC MEDIA

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

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

which is described in the accompanying complete specification. This applications is a Covention application and is based on the application numbered (3) P38 42 819.9 for a patent or similar protection made in (4) Federal Republic of Germany on 20th December 1988

~~My~~ Our address for service is WATERMARK PATENT & TRADEMARK ATTORNEYS
290 Burwood Road, Hawthorn, Victoria, Australia.

DATED this 18th day of December 19 89

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

(5) HOECHST AKTIENGESELLSCHAFT
by

D. B. Mischlewski
Registered Patent Attorney

To: THE COMMISSIONER OF PATENTS.

F013223 19/12/89
WATERMARK PATENT & TRADEMARK ATTORNEYS

R 2064

(CONVENTION. Company.)

Form 8

COMMONWEALTH OF AUSTRALIA

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

(hereinafter referred to as the applicant) for a Patent

(2) Here insert title of Invention.

for an invention entitled:(2) Process for separating organometallic compounds and/or metal carbonyls from their solutions in organic media

(3) Here insert full Name and Address, of Company official authorized to make declaration.

I,(3) KARL-HEINZ REICHELT
of 50 Brüningstrasse, D-6230 Frankfurt/Main 80, 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 20th day of December 1988, by HOECHST AKTIENGESELLSCHAFT

~~on the~~ XXXXXX ~~day of~~ XXXXXX ~~19~~ ~~by~~ XXXXXXXXXXXX

(5) Here insert (in full) Name and Address of Actual Inventor or Inventors.

3.(5) Dr. Helmut Bahrmann, Rohstr. 48, 4236 Hamminkeln-Brünen,
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~~is/~~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 the invention from the said actual inventors

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 Frankfurt/Main, Fed. Republic of Germany

this 19th day of October 1989

(6) Signature.

(6) (Dr. Karl-Heinz Reichelt
Procurist of
Hoechst Aktiengesellschaft)

To: THE COMMISSIONER OF PATENTS.

Edwd. Waters & Sons, Melbourne

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PROCESS FOR SEPARATING ORGANOMETALLIC COMPOUNDS AND/OR METAL CARBONYLS FROM THEIR SOLUTIONS IN ORGANIC MEDIA

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(56) Prior Art Documents
GB 1266180

(57) Claim

1. A process for separating organometallic compounds and/or metal carbonyls from their solutions in organic media, characterised in that the solutions are brought into contact with a semi-permeable membrane made of an aromatic polyamide (polyaramide).

621968

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

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Complete Specification Lodged:
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Complete Specification for the invention entitled:

PROCESS FOR SEPARATING ORGANOMETALLIC COMPOUNDS AND/OR METAL CARBONYLS FROM THEIR SOLUTIONS IN ORGANIC MEDIA

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

Process for separating organometallic compounds and/or metal carbonyls from their solutions in organic media

The invention relates to a process for separating by membrane filtration organometallic compounds and/or metal carbonyls dissolved in organic media, both classes of compounds being shortened to metal compounds in the following.

Organic compounds and carbonyl compounds of the transition metals, in particular compounds containing a metal of the platinum group as the central atom, are being increasingly used as catalysts in industrial chemical processes. The recovery of the catalyst has a considerable influence on the economy of these processes. It should be recovered as completely and as simply as possible.

Therefore there have been many attempts to develop techniques which satisfy these requirements. Two main routes have been pursued. The first restricts itself to recovering the catalyst metal and accepts the degradation of the catalytically active compound. Thermal cleavage, reduction, oxidation and precipitation steps dominate these processes. The aim of the other route is not to allow the catalytically active metal compound to be destroyed but to recover it undamaged so that it can be recycled to the process without any further work-up. The following deals in greater detail with this second variant for the recovery of organometallic compounds or metal carbonyls.

One possible route for separating organometallic coordination complexes from organic liquids consists in the use of selective separating membranes. Thus the DE-OS 19 12 380 describes a process in which the mixture of the complex with one or more organic components is brought into contact under pressure with one side of a cellulose membrane. The ratios of the molecular size and shape of the complex to molecular size and shape of the organic components are such that the material diffusing through the membrane has a reduced complex content.

The DE-OS 19 53 641 describes a process for separating organometallic compounds from a solution of the compounds in an organic solvent by means of a membrane. This procedure is characterised in that a silicone rubber membrane is used.

Furthermore, according to a process described in the GB-PS 12 66 180 organometallic compounds are removed from their solutions in organic solvents by means of a polyamide membrane.

Finally the DE-OS 24 14 306 describes the separation of organometallic compounds from organic solutions with a polyacrylonitrile membrane.

However, the afore-mentioned separating processes have the disadvantage that the membranes are not stable in the organic solvents, some of which are aggressive, in particular they swell when subjected to pressure and temperature loading and thus lose their beneficial properties. For this reason no membrane process for such separating tasks has been able to establish itself in industrial practice.

Therefore the task consisted in developing a process which permits the separation of organometallic compounds and/or metal carbonyls from organic media using membranes which not only exhibit the required separating properties under the selected operating conditions but also are highly stable and thus permit simple and effective separation of the organometallic compounds or the metal carbonyls from organic media.

The invention consists in a process for separating organometallic compounds and/or metal carbonyls from their solutions in organic media. It is characterised in that the solutions are brought into contact with a semi-permeable membrane made of an aromatic polyamide (polyaramide). The motive force behind the separating process can be either a difference in pressure (pressure filtration) or a difference in concentration (dialysis).

Surprisingly with the new process it is possible to recover organometallic compounds and/or metal carbonyls more or less completely and in unchanged form, i.e. without them being decomposed or changed in any other way. In this context it is particularly significant that the membrane does not lose its beneficial separating properties either through pressure or through temperature influences in the organic media.

In the sense of the present invention organometallic compounds are understood to be compounds in which carbon atoms of organic groups are bound to metal atoms. The metals also include the so-called semimetals such as boron and silicon as well as phosphorus. According to the invention organometallic compounds are also compounds soluble in an organic solvent in which the bond between the metal and carbon is formed by nitrogen, oxygen or sulfur. Examples of these compounds are acetyl acetonates and dimethylglyoximes.

The organometallic compounds, which also contain nitrogen and oxygen in addition to carbon, are preferably derived from the elements of the groups IVA, VA, VIA, VIIA, VIIIA and IB of the periodic table of the elements. Organometallic compounds of the elements manganese, cobalt, nickel, palladium, platinum, iridium and rhodium have special importance.

The term metal carbonyls is not restricted to compounds consisting solely of metal and CO but also covers the compounds which also contain other ligands such as hydrogen, olefins, phosphanes, acetate and benzonitrile. Suitable carbonyls are those of the metals of the groups VIA, VIIA and VIIIA of the periodic table, in particular carbonyls of iron, cobalt, nickel, ruthenium, rhodium and iridium.

The membranes used in accordance with the invention consist of an aromatic polyamide, also called polyaramide, and are already known. The polymers are also obtained by polycondensation from aromatic dicarboxylic acids or dicarboxylic acid derivatives and aromatic diamines in a dipolarly aprotic solvent. Suitable carboxylic acid components are, for example, terephalic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-diphenyletherdicarboxylic acid, 4,4'-diphenyl sulfone dicarboxylic acid or 2,6-naphthalene dicarboxylic acid.

Suitable diamine components are p-phenylene diamine, 3,3'-dimethoxybenzidine, 3,3'-dichlorobenzidine, 3,3'-dimethylbenzidine, 4,4'-diaminodiphenylmethane, 2,2-bis(4-aminophenyl)propane or 1,4-bis(4-aminophenoxy)-benzene.

Membranes of polyaramides containing various diamines as monomers in addition to a carboxylic acid component have gained special significance. Thus, for example, polyaramides synthetised from terephalic acid, p-phenylene diamine, 1,4-bis(4-aminophenoxy)benzene and 3,3'-dimethylbenzidine have proved successful. The amines can be statistically distributed in the polymers. The polyamides can, however, have the structure of block copolymers.

The average molecular weight of the polyaramides can range widely. Normally the range is 5,000 to 200,000. Polyaramides with a molecular mass of 10,000 to 50,000 are preferred.

A process which is described in the German patent application P 38 02 030 has proved successful for manufacturing the claimed membranes. The membranes disclosed in this publication consist of a copolyamide which is synthetised from three different diamines and a dicarboxylic acid. A solution of this copolyamide in an aprotic polar solvent of the amide type, e.g. N-methyl-2-pyrollidone, is spread onto a flat surface as a liquid layer. This liquid layer is added to the precipitating liquid, in particular water, which is miscible in the solvent of the solution but precipitates the polymer as a membrane. The precipitating liquid is left to act on the precipitated membrane until the solvent has been completely replaced by the precipitating liquid. If necessary, the membrane can be subjected to heat treatment. Then the membrane is dried, optionally after prior treatment with glycerin.

The membranes prepared according to the process described above are integrally asymmetric and are known in principle to one skilled in the art. The membranes have a very thin, active separating layer whose thickness is 0.05 to 5 μ and a porous supporting structure. The thickness of the membrane consisting of active separating layer and supporting structure can be 10 to 400 μ, it is preferably 50 to 200 μ.

The shape of the membrane can be selected at will. It can be a disc and in particular a hollow fibre or capillary, but can also have any shape suitable for the prescribed use. The decisive factor is to achieve maximum possible stability as possible and, moreover, as large a surface as possible per volume unit in order to attain a satisfactory throughput.

It is recommended to pretreat the membrane before use. In the simplest case it is immersed in the solution to be separated. However, other conditioning processes are also possible. If, for example, the membrane was prepared by precipitation with water, the water is replaced, e.g. by i-propanol by placing the membrane in i-propanol and replacing the alcohol several times. Then the i-propanol is replaced in the same manner by the organic medium in which the metal compounds to be separated are dissolved. The type and method of conditioning the membrane determine the operating conditions to be observed in the claimed process.

With a given dissolved metal compound, the decisive variables which can influence the separating process are the pressure applied, the temperature of the solution, the type of solvent and the concentration of the metal compound in the solution.

The separating procedure according to the claimed process can either be performed as pressure filtration or as dialysis. In the first case a pressure must be maintained between the retentate and the permeate sides of the membrane which is greater than the osmotic pressure of the system, i.e. of the solutions of different concentration on both sides of the membrane. It is expedient if the difference in pressure across the membrane is 0.1 to 15 MPa, preferably 0.1 to 10 MPa and in particular 0.2 to 2 MPa. In the second case a flushing solution is passed in countercurrent on the permeate side of the membrane. This process called dialysis is particularly advantageous in a hollow fibre or capillary module. Suitable flushing solutions are, for example, organic solvents. The operating temperatures of both process variants are 0 to 200°C and in particular 40 to 130°C.

The concentrations in the feed solution of the metal compounds to be separated can vary widely. The claimed process makes it possible to successfully separate dissolved metal compounds whose concentration is only a few ppm as well as metal compounds whose concentration is some per cent. However, it has proved expedient if the concentrations of the organometallic compounds and/or the metal carbonyls in the organic medium do not exceed 20 % by weight. With commercial processes feed solutions containing 2 to 400 wt. ppm of the metal compounds are of significance. They are used with particular success.

The linear flow velocity across the membrane ranges from 0.1 to 10 m/sec, preferably 0.5 to 2.5 m/sec.

The separating effect is probably due to the fact that the small components of the solution used, which depending on its origin contains, for example, unreacted starting materials, reaction products and, in some cases, a solvent or solvent mixture as a reaction medium, can diffuse through the active separating layer more easily than the metal compound. Thus, the greater the volume of the metal compound is and the greater the difference in size between the metal compound and the other components of the solution is, the better the separation is. It is expedient if the metal compound has at least a 50% larger cross-section than the largest organic component. To get a rough approximation the molecular weight of the components can be taken instead of the size of the molecule to assess the quality of the separation. It is advantageous if the difference in molecular weight between the metal compound and the organic components of the mixture is as great as possible.

The claimed process can be performed batchwise or continuously, in one or more stages. In general the membrane is located outside the reaction zone so that reaction conditions and separating conditions, e.g. pressure and temperature, can be optimised independently of each other.

With the one-step variant the feed solution is added to the membrane under pressure. In the simplest case the permeate is drawn off and the concentrated solution is removed from the separating device as soon as the desired concentration has been reached. This procedure can also be performed continuously to increase the separating efficiency. The feed solution then flows along the membrane, is concentrated and continuously drawn off, as is the permeate.

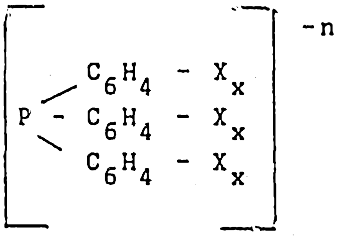
Multi-stage separation is performed with separating stages either in parallel or in series. The series configuration, in which the permeate is separated in every stage and the concentrated solution is passed to the next separating stage, permits particularly effective use of the available system pressure, i.e. the operating pressure in the previous process step, and permits the recovery of more highly concentrated solutions. If, on the other hand, the permeate is passed into consecutive separating stages, the dissolved substances can be more or less complately recovered regardless of the number of separating stages.

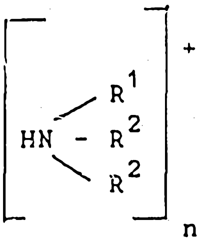
When using the process variants described above, the separating efficiency of the membrane can be further improved by increasing the flow rate over the membrane by means of a circulating pump.

Finally, by adding a flushing solution on the permeate side of the membrane in cocurrent and preferably in countercurrent to the feed side, the concentration of the dissolved substance in the permeate can be reduced and thus the motive force (difference in concentrations) increased (dialysis principle).

The new process has, inter alia, proved to be admirable for separating organometallic compounds and/or metal carbonyls from reaction solutions in which they have, for example, been used as homogeneous catalysts. The following metal complex compounds soluble in organic media and the reactions which are catalysed with them are given merely as examples of such compounds: Ni/Al complex compounds, e.g. $i\text{-}C_4H_9AlCl_2/NiCl_2[P(C_6H_5)_3]$ for the dimerisation of butadiene to trans-1,4-hexadiene and of butenes to octenes; Co/Al complex compounds, e.g. $i\text{-}C_4H_9AlCl_2/CoCl_2[P(C_6H_5)_3]_2$ for the dimerisation of butadiene to cis-1,4-hexadiene; phosphite-modified Ni/Al-alkyl compounds for the preparation of cyclooctadiene from butadiene; $Pd(CH_3COO)_2/P(C_2H_5)_3$ complex compounds for the preparation of octadiene-1,7; $RuHCl[P(C_6H_5)_3]_3$ or $RhCl(P(C_6H_5)_3]_3$ for the homogeneous hydrogenation of olefins; $RhCO[P(C_6H_5)_3]_2$ for the hydroformylation of formaldehyde;

$Ni[P(p\text{-}C_6H_4.CH_3)_3]_4/H^+$ for the hydrocyanation of butadiene; $Ir(COD)[P(C_6H_{11})_3]Py$ (COD = 1,5-cyclooctadiene, Py = pyridine) for the hydrogenation of cyclic alkenes; $RuCl_2[P(C_6H_5)_3]$ for the hydrogenation of terminal alkenes; $[Ru(BINAP)](ClO_4)_2$ (BINAP = 2,2'-bis(diphenylphosphino)1,1'-binaphthyl) for the asymmetric hydrogenation of olefinic double bonds; $HRhCO[P(C_6H_5)_3]_3$ for the hydroformylation of alpha-olefinic compounds such as allyl alcohol; $Pd[P(C_6H_5)_3]_4$ for the nucleophilic alkylation of allyl systems and the functionalising oligomerisation of butadiene; rhodium complex compounds such as $HRhCO[P(C_6H_5)_3]_3$ and those which contain triphenylphosphane or alkyl or aryl ammonium salts of sulfonated or carboxylated triarylphosphanes of the general formula:





as ligands. These compounds and their use are explained in slightly more detail in the following. However, it is naturally not intended to restrict the scope of the invention to the separation of this special compound class. In the above general formula X stands for a sulfonate(SO_3^-) or carboxylate radical(COO^-), x^1, x^2 and x^3 are 0 or 1, R^1, R^2 are each the same or different alkyl radicals having 4 to 12 carbon atoms or aryl or cycloalkyl radicals having 6 to 12 carbon atoms and R^1 also denotes hydrogen.

In such catalyst systems disulfonated and trisulfonated or dicarboxylated and tricarboxylated triphenylphosphanes are particularly suitable as ligand anions. The compounds do not need to be used in pure form but can also be used as a mixture of disubstituted and trisubstituted phosphane.

The cations of the ligands are derived from secondary or tertiary amines. Preference is given to amines containing a total of 16 to 36 carbon atoms. Examples are di-2-ethylhexylamine, diisooctylamine, diisononylamine, tri-n-octylamine, triisooctylamine, triisononylamine, triisodecylamine.

Apart from the phosphanes the rhodium complex compounds can contain other ligands such as H, CO amines, π-aromatics, e.g. cyclopentadienyl or π-olefins such as 1,5-cyclooctadiene.

Together with the phosphane ligand present in excess the rhodium compounds form a catalyst system which, homogeneously dissolved in the organic reaction medium, can, for example, be used in the hydroformylation of olefinically unsaturated compounds. The term olefinically unsaturated compounds covers straight-chain and branched olefins, regardless of the position of the double bond in the molecule, as well as cycloolefins such as n-hexene-1, n-heptene-1, n-octene-1, n-nonene-1, diisobutylene, tripropylene, cyclohexene, cyclooctene. The olefinically unsaturated compounds also include dienes such as 1,3-butadiene, 1,5-hexadiene and dicyclopentadiene as well as compounds containing functional groups such as acrylic acid, acrylic acid ester, acrylonitrile, methacrylic acid, methacrylic acid ester, vinyl ester, vinyl ether and acrolein.

The reaction mixture formed during the hydroformylation of the olefinic compound contains, for example, mainly the reaction product, an aldehyde, by-products such as the alcohol derived from the aldehyde as well as higher-boiling addition and condensation products of the aldehyde. Furthermore, a solvent serving as reaction medium can also be present.

Before the organic components of the reaction mixture are isolated, e.g. by distillation, the rhodium complex compound is generally separated. It is normally present in the mixture in a concentration of 1 to 1,000, in particular 3 to 400 and preferably 20 to 200 ppm. According to the new procedure it is now possible to almost completely separate the rhodium compound from the reaction product. In this connection it is particularly important that the rhodium compound is recovered in a form which permits its immediate re-use in the synthesis.

The following describes the preparation of a type of membrane which can be used in the process according to the invention. There is also a description of examples of the separation of organometallic compounds or metal carbonyls from reaction mixtures with said membrane using the new procedure.

Preparation of the membrane

The polyaramide is prepared by condensation of

97-99	mole %	terephthalic acid dichloride
25	mole %	p-phenylene diamine
25	mole %	1,4-bis(4-aminophenoxy)benzene
50	mole %	3,3'-dimethylbenzidine

in N-methylpyrrolidone as a solvent. Enough terephthalic acid dichloride is used for the polyaramide to have a Staudinger index of 200 to 300 ml/g. The amount of solvent is dosed so that a solution is formed containing about 7 % by weight polycondensate. After condensation has taken place, the hydrogen chloride loosely bound to the solvent is neutralised by the addition of 100 mole % CaO. Then 5 % by weight anhydrous calcium chloride (related to the polymer solution) is dissolved with stirring in the reaction mixture. The solution is gently warmed, filtered and degassed. It can be used directly for the preparation of the membrane.

It is possible to prepare the membrane without a support or on a polyester non-woven as a support. In the following the preparation of a support-free membrane is described. The slightly warmed polyaramide solution is spread onto a glass plate with a doctor blade to form a uniform film with a thickness of about 150 µ and then immersed in a water bath with a temperature of 2°C. After approximately 20 minutes the membrane is pulled off the glass plate and placed in hot water with a temperature of 100°C for 5 minutes. Then the membrane is placed in i-propanol to replace the pore liquid, water, with alcohol. Then the membrane is placed in toluene for approximately 10 hours, after this treatment it is suitable for performing separations. During all these operation care must be taken to ensure that the membrane does not dry out.

Example 1

The separation of the catalyst, which consists of a rhodium complex compound and the triisooctylammonium salt of tris(m-sulfophenyl)phosphane, from the raw product of the hydroformylation of dicyclopentadiene (DCP) is described below.

The separation is performed with 2,646 g of raw product which contains TCD-monoaldehyde and TCD-dialdehyde (TCD = tricyclodecane) in a weight ratio of 18 : 98.2, 24.8 ppm of rhodium (corresponding to 65.6 mg), a total of 698 ppm of phosphorus, i.e. P(III) and P(V) (corresponding to 1,8[illegible].9 mg) of which there are 17.4 mmoles of P(III)/kg (corresponding to 1,427.2 mg) as well as toluene as a solvent.

The raw product is passed at 40°C and a pressure of 0.5 MPa into a metal cell which is fitted with a membrane having a surface area of 20 cm^2 manufactured according to the above instructions. Any solution which does not diffuse through the membrane is circulated at a rate of approximately 8 l/h. The pass-over rate is approximately 0.15 m/sec.

After the experiment has been completed, 2,139.4 g of permeate (81 % of the feed) and 486.6 g of retentate (18.4 % of the feed) are obtained. The permeate contains a total of 357.3 mg of phosphorus (19.3 % of the feed), of which 172.4 mg as a P(III) compound (12.1 % of the feed) and 2.29 mg of rhodium (3.5 % of the feed). The retentate contains a total of 77.9 % phosphorus (related to the feed) and 95 % of the rhodium (related to the feed). The permeate flow is 12 l/(m^2 x h) at the beginning of separation and 5 l/(m^2 x h) at the end of the experiment.

Under the temperature and pressure conditions of the first separating stage 1,933 g of the permeate are subjected to a second membrane filtration. The permeate flow is 17.5 l/(m^2 x h) at the beginning of the experiment and 10 l(m^2 x h) at the end. The results of the separation are compiled in the following table:

Table 1

		permeate	retentate
amount	(% of feed)	73.1	7.2
P III	(% of feed)	8.8	13.1
Total P	(% of feed)	5.6	13.2
Rh	(% of feed)	0.4	4.3

Example 1 shows that when the claimed process is used, over 99.5 % of the rhodium and 94.4 % of the phosphorus(III) compound are retained.

Example 2

The combined retentates from example 1 are used as a catalyst for the hydroformylation of DCP in toluene as a solvent. After the reaction has been completed, GC analysis shows a conversion of 97.8 % and a ratio of monoaldehyde to dialdehyde of 2.0 : 98.0. At 40°C and a pressure of 0.5 MPa the permeate flow is 10.5 l/(m^2 x h) at the beginning and 3.6 l(m^2 x h) at the end of separation. The retention rates correspond to those of example 1.

Example 2 shows that according to the claimed process the catalyst system and the excess ligand can be separated and recirculated in their active forms.

Example 3

Solutions containing higher concentrations of metal complex compounds can also be successfully treated according to the new procedure. The product of the hydroformylation of DCP using the catalyst system of example 1 but with an Rh concentration of 102 ppm is used as a starting material. It contains TCD-dialdehyde, 16.5 mmoles of P(III)/kg, a total of 681 ppm of phosphorus and in addition toluene as a solvent.

Separation takes place under the temperature and pressure conditions and using the cell of example 1. In the first run the permeate flow is 10 $1/(m^2 \times h)$ at the beginning of the experiment and 3 $1/(m^2 \times h)$ at the end; in the second run in which the permeate of the first separation is used, 17 and 9 $1/(m^2 \times h)$.

The results of the separation are compiled in table 2.

Table 2

		permeate I/II		retentate I/II	
Amount	(g)	2,383.0	2,119	403.8	217
P^{III}	(% of feed)	12.9	8.7	67.0	12.3
Total P	(% of feed)	16.8	6.3	76.5	12.0
Rh	(% of feed)	2.5	0.2	96.3	2.9

Example 3 shows that the amount of metal and ligand retained does not fall even with higher rhodium concentrations.

Example 4

420 g of a product from the hydroformylation of hexadiene-1,5 with rhodium and triphenylphosphane as catalysts are separated according to the claimed process using the membrane cell of example 1. The Oxo raw product contains 333 ppm of Rh and 30 % toluene. The

ratio of monoaldehyde to dialdehyde is 15 to 85. The permeate flow at 40°C is 5 l/(m^2 x h).

The membrane filtration leads to the results compiled in table 3.

Table 3

	Permeate	Retentate
Amount (g)	137 (32.4 % of feed)	270 (67.5 % of feed)
Rh (ppm)	192 (19 % of feed)	400 (81 % of feed)

As can be seen, 80% of the rhodium contained in the raw product is separated.

The following examples prove the advantageous physical properties of the membrane used in accordance with the invention. A membrane with an average thickness of 270 µ manufactured and located in a cell according to the afore-mentioned regulations is used.

For separation the reaction mixture from the hydroformylation of DCP with rhodium and the triisooctylammonium salt of tris(m-sulfophenyl)phosphane as catalysts is used. The rhodium concentration in the Oxo raw product is 25.4 ppm, it also contains 23.4 mmoles in total of phosphorus/kg, 0.013 moles of P(III) and approximately 55 % toluene. The ratio of monoaldehyde to dialdehyde is 2 to 98. The amount of rhodium and phosphorus retained in the following examples 5 to 10 is roughly the same as in the experiments of example 1.

Example 5

For conditioning, the membrane is first measured for thickness, washed with acetone and then with isopropanol and then installed into the apparatus still moist from the isopropanol. Immediately afterwards, the apparatus is filled with toluene and the isopropanol is displaced from the membrane by washing it out.

Then the permeate flow is measured at 25°C and 0.3 MPa. It stabilises very quickly from 22 $l/(m^2 \times h)$ at the beginning to 18 to 19 $l/(m^2 \times h)$.

Example 6

In order to determine the permeate flow and the properties of the membrane compared with a rhodium and phosphane-free, raw TCD-dialdehyde from the hydroformylation of DCP, the toluene is displaced by a product freed from rhodium and phosphane by another means. The permeate flow of the membrane does not change.

This experiment shows that the membrane remains stable in the Oxo raw product, i.e. no swelling takes place.

Example 7

At 0.3 MPa and 25°C the membrane is fed with the Oxo raw product described above. Over a period of one hour the permeate flow is determined in 12 measurements. Immediately an average constant permeate flow of 5.7 $1/(m^2 \times h)$ establishes itself.

Example 8

At a pressure of 0.5 MPa but otherwise under the same conditions as in example 7, the permeate flow is determined in 6 individual measurements over a period of 30 minutes. An average value of 9.7 $1/(m^2 \times h)$ is determined. Example 8 shows an almost linear rise in the permeate flow with a pressure differential of 0.3 to 0.5 MPa.

Example 9

By gradually increasing the temperature from 25°C to 40°C the permeate flow rises continuously to 13.6 $1/(m^2 \times h)$. Thus its temperature coefficient is about +2.5%/°C.

Example 10

The raw product from the hydroformylation of DCP used in the previous examples is replaced again by toluene. The permeate flow rises spontaneously to 40 l/(m^2 x h) at 41°C and stabilises at 26 l/(m^2 x h) at 27°C and 0.5 MPa. After 1 hour the experiment is interrupted, the membrane removed and its thickness measured. There is almost no change in the thickness.

Example 10 shows that the membrane does not clog or foul and that it remains stable.

The examples 5 to 10 all prove the efficiency of the new process.

Example 11

The previously used membrane cell with a polyaramide membrane prepared according to the manufacturing process described above is fed with a C_9 aldehyde from the high-pressure hydroformylation of diisobutylene with rhodium. The rhodium content in the Oxo raw product (the metal being present as a carbonyl compound) is 4.3 ppm. The product contains no phosphorus. The permeate flow is 39 l/(m^2 x h) at the beginning of the experiment at 40°C and 0.5 MPa. It falls to 16.8 l/(m^2 x h) when there is a transition to the C_9 Oxo raw product in the first run and is 11.6 l/(m^2 x h) at the end of the experiment; the permeate flows in the second run (feed of the permeate of the first separation) are 14.5 and 10.1 l/(m^2 x h).

The results are compiled in table 4:

Table 4

	permeate 1	permeate 2	retentate 1	retentate 2
Amount(g)	625	517	132	104
Rh (% of feed)	52	18	35	27.9

After the experiment has been completed and the Oxo raw product replaced by toluene, a permeate flow of 40 l/(m^2 x h) is measured again.

~~Patent claims~~

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for separating organometallic compounds and/or metal carbonyls from their solutions in organic media, characterised in that the solutions are brought into contact with a semi-permeable membrane made of an aromatic polyamide (polyaramide).

2. A process according to claim 1, characterised in that the solutions are brought into contact with the semi-permeable membrane under a pressure differential across said membrane of 0.1-15 MPa.

3. A process according to claim 1, characterised in that the separation of organometallic compounds and/or metal carbonyls is performed as dialysis with the aid of the semi-permeable membrane.

4. A process according to one or more of the claims 1 to 3, characterised in that the membrane consists of a ~~statistic~~ statistically distributed or a block copolyaramide.

5. A process according to one or more of the claims 1 to 4, characterised in that the polyaramide is synthetised from terephthalic acid, p-phenylene diamine, 1,4-bis(4-aminophenoxy)benzene and 3,3'-dimethylbenzidine as monomer components.

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6. A process according to one or more of the claims 1 to 5, characterised in that the molecular weight given as the average weight of the polyaramide is 5,000 to 200,000, preferably 10,000 to 50,000.

7. A process according to one or more of the claims 1 to 6, characterised in that the membrane has the form of a capillary or a hollow fibre.

8. A process according to one or more of the claims 1 to 7, characterised in that the thickness of the separating layer of the membrane is 0.05 to 5 μ.

9. A process according to one or more of the claims 1 to 8, characterised in that the difference in pressure across the membrane is 0.1 to 15 MPa.

10. A process according to one or more of the claims 1 to 9, characterised in that the metal compounds are separated at temperatures of 0°C to 200°C, in particular 40°C to 130°C.

11. A process according to one or more of the claims 1 to 10, characterised in that [illegible] organometallic compounds are derived from metals of the groups IVA, VA, VIA, VIIA, VIIIA or IB of the periodic table.

12. A process according to claim 11, characterised in that the organometallic compounds are derived from manganese, cobalt, rhodium, iridium, nickel, palladium or platinum.

13. A process according to one or more of the claims 1 to 10, characterised in that the metal carbonyls are derived from metals of the groups VIA, VIIA or VIIIA of the periodic table.

14. A process according to claim 13, characterised in that the metal carbonyls are derived from iron, cobalt, nickel, ruthenium, rhodium or iridium.

15. A process according to one or more of the claims 1 to 14, characterised in that the concentration of the metal compounds in the solutions is 2 to 400 wt. ppm (related to the solution).

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