

1

3,437,431

RECOVERING PALLADIUM COMPOUNDS BY  
EXTRACTION WITH AMINES

Rolf Platz, Mannheim, Heinz Nohe, Ludwigshafen (Rhine), and Dominik Schuler, Mannheim, Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany  
No Drawing. Filed Dec. 22, 1965, Ser. No. 515,708  
Claims priority, application Germany, Dec. 28, 1964, B 79,910

Int. Cl. C01g 55/00

U.S. Cl. 23—50

6 Claims

## ABSTRACT OF THE DISCLOSURE

A process for recovering palladium compounds from aqueous solutions in which an amine containing at least six carbon atoms per nitrogen atom is placed in contact with said solution, the amine phase is separated, and the palladium compound is extracted therefrom with an aqueous acid. The process provides a highly advantageous method of recovering palladium compounds which process can be carried out continuously in which a high percentage of palladium is recovered.

This invention relates to a process for the recovery of palladium compounds from aqueous solution by extraction by means of amines.

Our copending application Ser. No. 294,262 relates to a process for the production of glyoxal by oxidation of ethylene with nitric acid in the presence of palladium compounds as catalysts. The reaction mixture obtained is an aqueous solution which in general contains 5 to 20% by weight of glyoxal, 0.01 to 3% by weight of palladium in the form of palladium compounds and 0.5 to 5% by weight of nitric acid. It is of great importance for the economy of the process for the palladium to be returned as quantitatively as possible. It is however not possible to separate the solutions by distillation because glyoxal is not distillable. Although the palladium compounds may be separated from the said solutions by means of ion exchangers or polyamide oximes, it has been found that the palladium compounds cannot be completely eluted. Sooner or later the ion exchanger or polyamide oxime therefore has to be destroyed if the palladium is to be recovered quantitatively. Moreover separation of palladium compounds with ion exchangers or polyamide oximes cannot be carried out continuously. It is also possible to precipitate the palladium quantitatively from the said solutions by means of complex-forming substances, such as salicyl aldoxime, but this is an analytical method and cannot be used on an industrial scale. It is also possible to reduce the palladium compounds by means of olefins, such as ethylene, but at the most 80% of the palladium can be recovered by this method and then as metal. The remainder of the palladium then has to be separated with ion exchangers or polyamide oximes, and this is attended by the said disadvantages.

Solutions of palladium compounds are also obtained in other catalytic processes, from which the palladium compounds have to be recovered, either as such or in the form of solutions which can be returned to the process. Even when it is possible to evaporate the solutions and thus to recover the palladium compounds, this is attended by high energy consumption because the palladium compounds are as a rule present in very low concentrations, usually less than 1% by weight.

2

We have now found that palladium compounds can be advantageously recovered from aqueous solutions, which may be acid, by extracting the palladium compounds with amines containing at least six carbon atoms for each nitrogen atom, with or without the coemployment of inert solvents having very little or no miscibility with water, separating the amine phase and reextracting the palladium compounds therefrom with aqueous acids, the amount and/or concentration of the said aqueous acids being higher than in the original aqueous, possibly acid, solutions of the palladium compounds so that the activity of the  $\text{Pd}^{2+}$  ions in the said aqueous acid is less than that in the said aqueous solutions.

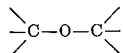
The process according to this invention makes possible a simple and industrially convenient recovery of palladium compounds from aqueous solutions by transferring them into other solutions. The process is preferably used where the object is to separate palladium compounds from solutions such as are obtained by catalytic processes, i.e. solutions which either contain other valuable substances and/or impurities which impair direct reuse as catalyst solution. The solution into which the palladium compounds are transferred are then capable of being used directly as catalyst solution again. The process requires only little energy, the palladium compounds are recovered to a very large extent and the process may be carried out continuously without difficulty. It is of particular importance in the production of glyoxal by the process described in the copending application mentioned above. Surprisingly the yield of glyoxal is not impaired although it is known that glycolic acid is formed from glyoxal under the influence of bases by the Cannizzaro reaction and that primary and secondary amines will react with aldehydes.

Palladium compounds which may be recovered by the new process are for example palladium salts of organic and inorganic acids, such as palladium chloride, palladium bromide, palladium iodide, palladium sulfate, palladium nitrate and palladium acetate. In aqueous solutions, such as in general occur in catalytic processes, the palladium is present at least partly as an anion complex, for example as the complex  $[\text{PdCl}_4]^{2-}$ . The palladium compounds may be present in very low concentration, for example 0.0005% by weight reckoned as palladium. The upper limit of the concentration is not critical, but solutions containing more than 5% by weight hardly ever occur.

The palladium compounds are present in aqueous solutions which may be acid. The term aqueous solutions is intended to include solutions having a water content of at least 50%, preferably at least 80%, by weight. In addition to the palladium compounds the said aqueous solutions may contain up to 50%, preferably up to 20%, by weight of organic or inorganic components. Organic components are, for example, aldehydes, such as glyoxal, or organic acids, such as formic acid or acetic acid, the said organic acids being usually present in amounts less than 5% by weight. Inorganic components are, for example, inorganic salts or inorganic acids, for example hydrochloric acid, nitric acid, sulfuric acid and/or phosphoric acid. The concentration of the inorganic acids in the aqueous acid solutions is in general less than 20% by weight.

Amines which are particularly suitable for the new process are primary, secondary or tertiary amines having six to sixty, particularly twelve to thirty-five, carbon atoms. They may contain alkyl, alkenyl, cycloalkyl, aryl, aralkyl or heterocyclic radicals as substituents and 1 to 3 nitrogen atoms in the molecule. They may also be derived from cyclic imines, such as morpholine or pyrrolidine. Groups or atoms which the inert or substantially

inert under the extraction conditions, for example halogen atoms or ether groups, i.e.



may furthermore be contained in the said radicals. The following specific amines are given by way of example: n-octylamine, isododecylamine (mixture of isomers derived from tetrameric propylene), bis-tridecylamine, tris-isooctylamine, tris-octadecylamine, methyl-bis-octylamine, isobutyl-bis-octylamine, isobutyl-bis-tridecylamine, N,N-dibutylaniline, N,N-diethylbenzylamine, N,N-dibutylcyclooctylamine, 2-butylaminopyridine, N-2-ethylhexylpyrrolidine, N - dodecylmorpholine, N - hexylthiomorpholine, N,N,N',N'-tetrabutylethylene diamine, tridecylamine, oleylamine, bis-2-ethylhexylamine and dimethylstearlylamine.

It is possible to use the amines together with inert water-immiscible solvents. This is recommendable particularly when an amine is used which within the specified range has a small number of carbon atoms per nitrogen atom, or when the amine is solid or highly viscous at the working temperature. Examples of suitable solvents are hydrocarbons, such as benzene, toluene, xylene and liquid petroleum fractions; and halohydrocarbons, such as chloroform, ethylene chloride, trichloroethylene and chlorobenzene. The solvent is advantageously used in such an amount that the content of amine is above 3%, preferably from 3 to 20% by weight. A solvent may also be used for subsequent extraction of amines from the aqueous phase.

The amount of amine which is used for extraction of the palladium compounds depends on various factors and may vary within wide limits. It depends for example on the type and concentration of the palladium compound and of any acid present, on the type of amine and on whether the extraction is carried out in one or more stages. It also depends on whether other substances are present in the solution. It is recommended that the most favorable amount of amine for given conditions should be ascertained in a preliminary experiment. In the case of solutions obtained in the said process for the production of glyoxal from ethylene, and which usually contain 3 to 20% by weight of glyoxal, 0.1 to 10% by weight of nitric acid and 0.002 to 1.0% by weight of palladium compounds, reckoned as palladium, the amount of amine used, either as such or dissolved in an inert solvent, is in general 0.1 to 10 times the weight of the said solutions.

Aqueous acids, particularly aqueous mineral acids, are used for the reextraction. For example 10 to 60% by weight hydrochloric acid, sulfuric acid, phosphoric acid or nitric acid may be used. If the palladium compound is to be used as catalyst for the said production of glyoxal from ethylene, it is best to use 15 to 60% by weight nitric acid.

For a practically complete transfer of the palladium compound from the amine phase to the aqueous acid, it is important that the acid contained in the aqueous acid should be used in an amount larger than that of any acid contained in the original aqueous solution of the palladium compound and/or that the concentration of the aqueous acid should be higher than the acid concentration in the original aqueous solution (if it contains any acid at all). More particularly, transfer of the palladium compound from the original solution into the aqueous acid is only possible if the activity of the  $\text{Pd}^{2+}$  ions in the aqueous acid is lower than in the original solution, and concentrations and amounts of acids contained in the original aqueous solutions and in the aqueous acid into which the palladium compounds are to be transferred have to be chosen accordingly. In order to keep expenditure for extraction as low as possible, the activity of the  $\text{Pd}^{2+}$  ions in the aqueous acid should be at least 20% less than in the original solution. The activity of the  $\text{Pd}^{2+}$

ions in the original solution may readily be determined with a galvanic cell. The activity of the  $\text{Pd}^{2+}$  ions in the aqueous acid may be kept low by using large volumes of aqueous acids having not too low a concentration.

Large volumes naturally result in high dilution, and high acid concentrations cause a decrease in the  $\text{Pd}^{2+}$  concentration in favour of the said aniono complexes. The amount of aqueous acid required, and its concentration, can only be calculated with difficulty. It is simplest if the same acid is present in the aqueous acid as in the original solution. It is best however in this case as well to determine the most favorable amounts and concentrations in a preliminary experiment. Amounts and concentrations of acid in the original aqueous phase and in the aqueous acid are considered to be a favorable relation if substantially all of the palladium compound is transferred into the aqueous acid in at the most 6 theoretical stages.

The process is preferably carried out at room temperature. Sometimes it is advantageous to use temperatures up to about 60° C., particularly in cases where the extractant is rather viscous and coemployment of an inert water-immiscible solvent is not desired. The temperature range between 0° and 60° C. covers all cases of importance.

The new process may be carried out in the conventional continuous or batch extraction apparatus. The number of theoretical stages may vary within wide limits. It naturally depends to a great extent upon the palladium content in the original solution or in the amine phase to which the extraction is to be carried. Sometimes only one or two stages are sufficient. In other cases it is very much higher. In the recovery of palladium compounds from the said reaction mixtures which are obtained in the production of glyoxal from ethylene, two to ten theoretical stages are generally sufficient.

The invention is illustrated by the following examples in which parts are parts by weight unless stated otherwise. The parts by weight bear the same relation to parts by volume as the g. to the ml.

#### Example 1

800 parts by volume of an aqueous solution which contains in 1,000 parts by volume 7 parts of nitric acid and 0.36 part of palladium in the form of palladium nitrate as well as small amounts of aldehydes and organic acids is extracted per hour countercurrently with 1,250 parts by volume per hour of a mixture obtained by making 6 parts by weight of isododecylamine up to 100 parts by volume with trichloroethylene, in an extraction apparatus consisting of six mixing and separating vessels. After this extraction, the extracted solution contains only 0.00067 part of palladium in 1,000 parts by volume. The amine solution containing palladium is separated and subjected in a second extraction apparatus of the same type to extraction countercurrent with 500 parts by volume per hour of an aqueous solution containing 50 parts of nitric acid in 100 parts by volume. More than 99% by weight of the palladium contained in the amine solution is thereby transferred to the nitric acid solution.

The solution of palladium in nitric acid obtained may be used direct for the oxidation of ethylene.

#### Example 2

The procedure of Example 1 is followed but 1,000 parts by volume per hour of a solution of 100 parts of bis-tridecylamine in 900 parts of toluene is used for the extraction. In this case, too, more than 99% of the palladium is recovered by reextraction of the amine solution containing palladium with the nitric acid solution described in Example 1.

#### Example 3

900 parts by volume per hour of an aqueous solution containing in 1,000 parts by volume 20 parts of nitric acid, 0.52 part of palladium, 98 parts of glyoxal and small amounts of organic contaminants (carboxylic acids and

5

aldehydes) and also, countercurrent thereto, 600 parts by volume per hour of a mixture obtained by making up 10 parts of isobutyl-bis-tridecylamine to 100 parts by volume with toluene, are supplied to an extraction column having a length of 2 meters. The extracted solution contains a residual amount of only 0.0002 part by weight of palladium in 1,000 parts by volume. The amine solution containing palladium which has been separated from the aqueous phase is extracted countercurrent in another extraction column of the same type with 900 parts by volume per hour of an aqueous solution containing 35 parts of nitric acid in 100 parts by volume. When the nitric acid leaves the column it contains 0.52 part of palladium in 1,000 parts by volume. The mixture of amine and toluene is recycled through the two columns.

#### Example 4

900 parts by volume per hour of an aqueous solution containing, in 1,000 parts by volume, 110 parts of glyoxal, 0.75 part of palladium, 25 parts of pure nitric acid and small amounts of organic acids and aldehydes is extracted in an extraction column having a length of 3 meters with 800 parts by volume per hour of a mixture obtained by making up 8 parts of triisooctylamine with o-xylene to 100 parts by volume. The amine solution containing palladium is separated and reextracted in an extraction column of the same type with 800 parts per hour of aqueous 35% nitric acid. The extracted solution leaving the first column contains 0.00086 part of palladium in 1,000 parts by volume. The nitric acid in which the palladium has accumulated and leaving the second column contains, in 1,000 parts by volume, 0.84 part of palladium and may be used for oxidizing ethylene.

We claim:

1. A process for recovering palladium compounds from an aqueous solution which comprises extracting said palladium compounds from said aqueous solution with an amine containing at least 6 carbon atoms per nitrogen atom, said amine being at least substantially water-insolu-

6

ble, separating the amine phase and re-extracting therefrom said palladium compound with an aqueous acid, the amounts and concentrations of acid contained in said aqueous solution and in said aqueous acid being chosen so that the activity of the  $\text{Pd}^{2+}$  ions in the said aqueous acid is less than the activity of the  $\text{Pd}^{2+}$  ions in said aqueous solution.

2. A process as claimed in claim 1, wherein said palladium compounds are palladium salts of organic or inorganic acids.

3. A process as claimed in claim 1, wherein the concentration of the palladium compounds in said aqueous solution is between 0.0005% by weight and 5% by weight.

4. A process as claimed in claim 1, wherein the concentration of the palladium compounds in said aqueous solution is between 0.002% by weight and 1% by weight.

5. A process as claimed in claim 1, wherein an inert solvent immiscible with water is coemployed.

6. A process as claimed in claim 1, wherein said aqueous solution contains 5 to 20% by weight of glyoxal, 0.01 to 3% by weight of palladium in the form of palladium compounds and 0.5 to 5% by weight of nitric acid.

#### References Cited

##### UNITED STATES PATENTS

|           |         |          |         |
|-----------|---------|----------|---------|
| 2,909,542 | 10/1959 | Soloway  | 23—22 X |
| 3,088,798 | 5/1963  | Fetscher | 23—87 X |
| 3,197,274 | 7/1965  | White    | 23—340  |

##### OTHER REFERENCES

Coleman et al.: "Industrial & Engineering Chemistry," vol. 50, December 1958, pp. 1756-1762.

HERBERT T. CARTER, *Primary Examiner*.

U.S. Cl. X.R.

23—87, 102, 105, 117; 280—429