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(54) Title: PROCESS FOR THE RECOVERY OF PHOSPHATE VALUES FROM A WASTE SOLUTION

(57) Abstract: Process for the recovery of phosphate values from a waste solution Process for the recovery of phosphate values from a waste solution containing heavy metals and at least 25 % in weight phosphoric acid, wherein the waste solution is contacted with a reactant able to form an insoluble phosphate salt by reaction with the phosphoric acid contained in the solution, the insoluble phosphate salt is separated and the separated phosphate salt is dried and valorised or alternately converted back to phosphoric acid.

Process for the recovery of phosphate values from a waste solution

This application claims priority to European patent application EP 09160061, the whole content of this application being incorporated herein by reference for all purposes.

The invention relates to the recovery of phosphate values out of waste solutions containing spent phosphoric acid, in particular out of waste solutions produced in aluminium treatment processes, more particularly in aluminium etching processes using phosphoric acid.

Phosphoric acid is a widely used industrial chemical product. Huge amounts of ultra pure phosphoric acid are consumed in the electronic industry ("electronic grade"), leading to high quantities of phosphate containing waste solutions. Especially, the LCD industry uses yearly more than 100kT of phosphoric acid containing solutions, as aluminium etchants. Electronic grade phosphoric acid has typically the following basic properties :

Formula	H_3PO_4
Molecular weight (g)	98.0
Typical conc. (%)	80 - 85
P content (%)	31.3
Density 85% (g/ml)	1.71
Density 100% (g/ml)	1.88
mp (°C), 85%	21.0
mp (°C), 100%	42.3
CAS-No	7664-38-2

Table 1

WO2005/120675 describes a process for treating etching wastes containing phosphoric acid, acetic acid and nitric acid. This process appears however to be difficult and costly to apply.

The invention aims to furnish a process for the recovery of phosphate values out of waste solutions, which is simple and cost effective, whereas capable of valorising the phosphate values contained in waste solutions having low concentrations of phosphoric acid and containing high amount of different impurities.

In consequence, the invention concerns a process for the recovery of phosphate values from a waste solution containing heavy metals and at least

25 % in weight phosphoric acid wherein the waste solution is contacted with a reactant able to form an insoluble phosphate salt by reaction with the phosphoric acid contained in the solution, the insoluble phosphate salt is separated and the separated phosphate salt is dried and valorised.

In the process according to the invention, the waste solution contains heavy metals. Examples of heavy metals are aluminium, cadmium, lead, mercury. The process according to the invention is especially suitable to waste solutions containing aluminium. The waste solution contains advantageously at least 10 ppm in weight, preferably at least 50ppm of heavy metals, in particular of aluminium. It is recommended that it contains at most 1%, preferably 0.5%, more preferably at most 1000 ppm of heavy metals, in particular of aluminium.

The waste solution contains at least 25% in weight, preferably at least 40 %, more preferably at least 50%, in some instances most preferably at least 60% phosphoric acid. Advantageously this percentage does not exceed 90%, preferably 85%, more preferably 80%, most preferably 70%. The process according to the invention can however also advantageously recover phosphate values out of waste solutions containing less than 60%, in some instances less than 50%, even less than 40% phosphoric acid.

In the process according to the invention, the waste solution is contacted with a reactant able to form an insoluble phosphate salt. It is recommended that the reactant is added to the solution in an amount comprised between 0.75 and 1.5, preferably between 0.85 and 1.25 times the stoichiometric amount necessary for the reaction of all the phosphoric acid present in the solution. The amount is preferably approximately equal to the stoichiometric amount.

The insoluble phosphate salt can by separated by any suitable separation method allowing to separate solids out of liquids, as for instance filtration. The separated phosphate salt is then preferably washed. After optional drying, the washed separated phosphate salt is valorised. The valorisation includes preferably packing and sale.

The process according to the invention allows to recover generally more than 80%, advantageously more than 90%, preferably more than 95% of the phosphate values of the waste solution.

The process is particularly effective to recover phosphate values from waste solutions containing, besides phosphoric acid, other acids.

In one advantageous embodiment, the waste solution contains at least 1%, preferably more than 5%, more preferably more than 10%, most preferably more than 20% nitric acid.

In another advantageous embodiment, the waste solution contains at least 1%, preferably more than 5%, more preferably more than 10%, most preferably more than 20% acetic acid.

In still another advantageous embodiment, the waste solution contains both at least 1% nitric acid and at least 1% acetic acid. All the different ranges of nitric and acetic acids of the previous embodiments can advantageously also be combined.

In a preferred embodiment of the process according to the invention, the waste solution is produced by an aluminium etching process. Such waste solution is the corrosive waste coming from the etching process of, for instance, semiconductor manufacturing plants. This waste solution comprises phosphoric acid, nitric acid and acetic acid, aluminium and some other metallic impurities. In semiconductor manufacturing, the etching process is carried out several times to accomplish the controlled removal of thin films from the wafer surface. The etching can be done with liquid or gaseous etchants. Liquid etchants (wet etching) produce oxidation reactions. The ability to oxidize the metal and the solubility of the resulting species are critical in the wet etching of metals. In the case of aluminium, wet etching is commonly done with a mixture of phosphoric acid (H_3PO_4), nitric acid (HNO_3) and acetic acid (CH_3COOH) in water. Nitric acid is used to oxidize the surface of the aluminium. Phosphoric acid then dissolves the aluminium oxide layer and the process can further progress. Acetic acid and water act only as diluents to keep the aluminium salt into solution.

Table 2 shows some typical aluminium etchants based on phosphoric acid:

Concentrations	Etchants
19 : 1 : 1 : 2	H_3PO_4 : HAc : HNO_3 : H_2O
3 : 1 : 3 : 1	H_3PO_4 : HAc : HNO_3 : H_2O
4 : 4 : 1 : 1	H_3PO_4 : HAc : HNO_3 : H_2O
15 : 0 : 1 : 1-4	H_3PO_4 : HAc : HNO_3 : H_2O

Table 2

The H_3PO_4 concentration is usually between 30% and 65% H_3PO_4 while the aluminium content is preferably less than 0.1 %, more preferably less than 500 ppm.

In the process according to the invention, it is essential that the reactant is able to form an insoluble phosphate salt, which can be easily separated.

In recommended embodiments, the reactant contains calcium and is able to form an insoluble calcium phosphate salt by reaction with phosphoric acid. Such reactant is preferably calcium hydroxide or calcium carbonate. In preferred variants of those embodiments, the insoluble calcium phosphate salt, which is valorised in the process according to the invention, is preferably dicalcium phosphate. Dicalcium phosphate (calcium monohydrogen phosphate - $CaHPO_4$ - DCP) is a commercial product which has in its own different applications, for instance in animal feed.

In those preferred variants of the recommended embodiments, the amount of reagent is advantageously added in a controlled manner, in order to reach a pH of at least 4, preferably 5.

Whereas the valorised insoluble phosphate salt can have a variety of uses in itself, as is in particular the case for DCP, in the most preferred embodiments of the invention, the insoluble phosphate salt, in place of being washed, dried and valorised, is further reacted with a strong acid in order to produce recovered phosphoric acid and another insoluble salt.

In some instances, the insoluble phosphate salt can however be advantageously washed before being reacted with the strong acid, in order to further remove impurities from the surface of the salt particles.

In those most preferred embodiments, the waste solution contains also advantageously other acids, preferably nitric and/or acetic acid, particularly in the different ranges described hereabove.

In recommended variants of those most preferred embodiments, the strong acid is sulphuric acid and the other insoluble salt is calcium sulphate.

The recovered phosphoric acid is advantageously further purified by contact with ion exchange resins and/or by melt crystallisation.

Ion exchange resins allow particularly easy removal of cationic impurities. Preferred resins comprise:

- strong acidic resins (A200 Rohm&Haas);
- chelating macroporous resins comprising imino-di-acetate groups, which appeared especially suitable for the removal of copper (S 930 Purolite);
- chelating macroporous resins comprising amino-phosphoric acid groups (S 950 Purolite), especially suitable for the removal of divalent cations like Ca, Mg but also for Cu, Pb;

- macroporous strong acidic resin (C160 Purolite).

Melt crystallation refers to the purification techniques described by G.F.Arkenbout ("Melt Crystallization Technology" Technomic publishing company, 1995). Use of hydraulic wash columns as described in US6495044 is particularly recommended.

Those advantageous embodiments, in particular those involving melt crystallisation with hydraulic wash columns are especially suitable for the production of electronic grade phosphoric acid.

Typical composition of electronic grade phosphoric acid is given in Table 3.

H_3PO_4 (86%)	85.0-87.0%
Nitrate (NO_3)	5 ppm max
Total Sulfur (as SO_4)	12 ppm max
Chloride (Cl)	1 ppm max
Aluminium (Al)	0.5 ppm max
Antimony (Sb)	1 ppm max
Arsenic (As)	0.05 ppm max
Calcium (Ca)	1 ppm max
Chromium (Cr)	0.2 ppm max
Cobalt (Co)	0.05 ppm max
Copper (Cu)	0.05 ppm max
Gold (Au)	0.3 ppm max
Iron (Fe)	1.0 ppm max
Lead (Pb)	0.3 ppm max
Lithium (Li)	0.1 ppm max
Magnesium (Mg)	0.2 ppm max
Manganese (Mn)	0.1 ppm max
Nickel (Ni)	0.2 ppm max
Potassium (K)	1 ppm max
Sodium (Na)	1 ppm max
Strontium (Sr)	0.1 ppm max
Titanium (Ti)	0.3 ppm max
Zinc (Zn)	1.0 ppm max

Table 3

The example which will be now described illustrates the invention.

Example

Etching solution:

A synthetic etching solution has been prepared in the following way. In a beaker, 14.5 grams of nitric acid 65 % (w/w), 269.5 grams of phosphoric acid 85 % (w/w) and 16 grams of acetic acid 100 % have been mixed. The solution so obtained contains (by weight) : 3.1 % nitric acid, 76.4 % phosphoric acid, 5.3 % acetic acid and 15.2 % water.

DCP precipitation ($H_3PO_4 + Ca(OH)_2 \rightarrow CaHPO_4 + 2\ H_2O$) (1):

150 grams of this etching solution have been introduced in a 2 litre beaker comprising a stirrer, a temperature probe and a pH probe. A milk of lime solution containing 69 g of calcium per kilogram has been added slowly (30 to 40 grams per minute). The addition was stopped when the pH probe showed a pH of 5. No cooling neither heating was done. Due to the exothermic reaction, temperatures raised from 26 °C (beginning of experiment) to 69 °C (end of experiment). The precipitate formed during the reaction was matured for 2 hours. It was then filtered and washed with deionised water. Finally, it was dried at 60 °C. 162 grams of dried precipitate were obtained, extremely close to the theoretical 100% yield of the reaction (163 grams).

The analysis of the precipitate and the analysis of the solution left after precipitation (filtrate) have shown that the precipitate contains equimolar quantities of calcium and phosphate (as expected for $CaHPO_4$) in such quantities that the yield is over 95 %.

Phosphoric acid regeneration ($CaHPO_4 + H_2SO_4 + x\ H_2O \rightarrow H_3PO_4 + CaSO_4.xH_2O$) (2):

140 grams of the precipitate obtained above were mixed with 370 grams of water in a 1 litre stirred beaker. 105.4 grams of sulphuric acid 96 % (w/w) were added slowly.

After 30 minutes, the precipitate formed during the reaction was filtered and washed with deionised water. It was then dried at 60 °C. In the end, 154 grams of dried precipitate and 194 grams of filtrate were obtained. The analysis of the precipitate showed that the precipitate contains equimolar quantities of calcium and sulphate, as expected for $CaSO_4$ according to equation (2), in such quantities that the yield of the reaction, expressed as sulphate precipitation, is over 95 %. The analysis of the filtrate showed that the final solution contains more than 95 % of the phosphate originally present in the solid DCP and no

more than 1 % of sulphate. This confirms that the yield of the reaction, expressed as phosphate conversion to phosphoric acid is over 95 %, in agreement with the results observed for the precipitate.

The example described above illustrates the high yield of the conversion of the phosphate contained in a typical aluminium etching solution into a solution containing almost only phosphoric acid.

CLAIMS

1. Process for the recovery of phosphate values from a waste solution containing heavy metals and at least 25 % in weight phosphoric acid wherein the waste solution is contacted with a reactant able to form an insoluble phosphate salt by reaction with the phosphoric acid contained in the solution, the insoluble phosphate salt is separated and the separated phosphate salt is washed, dried and valorised.

2. Process according to claim 1, wherein the waste solution contains at least 100ppm in weight aluminium.

3. Process according to claim 2, wherein the waste solution is produced by an aluminium etching process.

4. Process according to any of the preceding claims, wherein the waste solution contains at least 1% in weight nitric acid.

5. Process according to any of the preceding claims, wherein the reactant is able to form an insoluble calcium phosphate salt by reaction with phosphoric acid.

6. Process according to any of the preceding claims, wherein the reactant is calcium hydroxide or calcium carbonate

7. Process according to any of the preceding claims, wherein the insoluble calcium phosphate salt is dicalcium phosphate.

8. Process according to any of the preceding claims, wherein the insoluble phosphate salt in place of being washed, dried and valorised is further reacted with a strong acid in order to produce recovered phosphoric acid and an other insoluble salt.

9. Process according to the preceding claim, wherein the strong acid is sulphuric acid and the other insoluble salt is calcium sulphate.

10. Process according to any of claims 8 or 9, wherein the recovered phosphoric acid is further purified by contact with ion exchange resins and/or by melt crystallisation.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B25/32 C23F1/46
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B C23F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2005/120675 A1 (DAEIL DEV CO LTD [KR]; KIM HO-SUK [KR]; AHN JAE-WOO [KR]; KIM JU-YUP [) 22 December 2005 (2005-12-22) cited in the application paragraph [0003] -----	1-7 8-10
X	DATABASE WPI Week 198422 Thomson Scientific, London, GB; AN 1984-137263 XP002602454 & JP 59 070779 A (CRYSTAL ENG KK) 21 April 1984 (1984-04-21) * abstract -----	1
Y	US 3 425 799 A (HAZEN WAYNE C ET AL) 4 February 1969 (1969-02-04) claims ----- -/--	8-10

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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4

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 089 681 A (FISONS LTD) 1 November 1967 (1967-11-01) page 1, line 11 - line 24	7
A	US 3 634 029 A (AMANRICH ROBERT) 11 January 1972 (1972-01-11) claims; examples	1-10
A	EP 0 394 748 A2 (HOECHST AG [DE]) 31 October 1990 (1990-10-31) examples	1-10

4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2010/056405

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005120675 A1	22-12-2005	KR 20050003996 A	12-01-2005
JP 59070779 A	21-04-1984	JP 1430931 C	24-03-1988
		JP 62039236 B	21-08-1987
US 3425799 A	04-02-1969	NONE	
GB 1089681 A	01-11-1967	NONE	
US 3634029 A	11-01-1972	BE 723436 A	16-04-1969
		CH 488626 A	15-04-1970
		DE 1807623 A1	12-06-1969
		ES 359601 A1	16-06-1970
		GB 1236610 A	23-06-1971
		IL 30821 A	30-08-1972
		NL 6815725 A	09-05-1969
		NO 120584 B	09-11-1970
		SE 341621 B	10-01-1972
EP 0394748 A2	31-10-1990	DE 3913853 A1	31-10-1990
		US 4971778 A	20-11-1990