

PATENT DECLARATION FORM
(CONVENTION OR NON-CONVENTION)

DECLARATION IN SUPPORT OF APPLICATION FOR A PATENT

No. 27128/88

Insert name of applicant.

In support of the application/made by METALEUROP S.A.

Insert title of invention.

for a patent for an invention entitled: PROCESS FOR THE HYDROMETALLURGICAL TREATMENT OF A SOLUTION OF MATERIALS CONTAINING GALLIUM

Insert full name(s) and address(es) of person(s) making declaration. If applicant a company, person must be authorised to make declaration.

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Delete alternatives which do not apply

do solemnly and sincerely declare as follows:

- 1. (a) I am/We are the applicant(s) for the patent.
- OR (b) I am authorized by the abovementioned applicant to make this declaration on its behalf.
- 2. (a) I am/We are the actual inventor(s) of the invention.
- OR (b) Yves LE QUESNE
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Insert name(s) and address(es) of actual inventor(s).

is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:-

The said applicants are the assignees of the invention and of the priority right from the actual inventor

Insert details of entitlement to apply, e.g. Applicant is assignee of inventor(s)

Delete 3 and 4 if application non-convention. Otherwise insert details of basic application(s).

- 3. The basic application(s) as defined by Section 141 of the Act was/were made in the following country or countries on the following date(s) by the following applicant(s)
in FRANCE on November 24, 19 87
by the applicant no. 87 16291
- in _____ on _____ 19 _____
- by _____
- in _____ on _____ 19 _____
- by _____
- in _____ on _____ 19 _____
- by _____

- 4. The basic application(s) referred to in paragraph 3 of this Declaration was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

Place and date of Signature.

Declared at Fontenay-sous-Bois this 30th day of September 19 89

NO ATTESTATION OR SEAL

J.M. Demarthe
Jean-Michel DEMARTHE
Managing Director
Signature(s) of declarant(s).

To: The Commissioner of Patents,
Australia

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- (57) Claim

1. Process of hydrometallurgical treatment of a solution of materials containing gallium comprising in addition at least one metalloid from Group V of the periodic table of the elements, characterized in that it comprises the following steps:

- b) adjustment of the concentration of chloride ions and of the acidity of the said solution by addition of hydrochloric acid and an alkali metal chloride or an alkaline earth metal chloride;
- c) placing the said solution in contact with an organic phase comprising at least one neutral pentavalent phosphorus compound having a phosphorus-oxygen double bond.

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<p>(21) Numéro de la demande internationale: PCT/FR88/00574 (22) Date de dépôt international: 24 novembre 1988 (24.11.88) (31) Numéro de la demande prioritaire: 87/16291 (32) Date de priorité: 24 novembre 1987 (24.11.87) (33) Pays de priorité: FR (71) Déposant (pour tous les Etats désignés sauf US): META-LEUROPS S.A. [FR/FR]; Le Péripole 1, 58, rue Roger-Salengro, F-94120 Fontenay-sous-Bois (FR). (72) Inventeur; et (75) Inventeur/Déposant (US seulement) : LE QUESNE, Yves [FR/FR]; 35, rue Mathurin-Régnier, F-75015 Paris (FR). (74) Mandataire: MARTIN, Jean-Jacques; Cabinet Regimbeau, 26, avenue Kléber, F-75116 Paris (FR).</p>		<p>(81) Etats désignés: AU, FI, JP, NO, US. Publiée <i>Avec rapport de recherche internationale.</i></p> <div data-bbox="880 712 1273 855" style="border: 1px solid black; padding: 5px; text-align: center;"><p>This document contains the amendments made under Section 49 and is correct for printing.</p></div>
<p>(54) Title: PROCESS FOR HYDROMETALLURGICAL TREATMENT OF A SOLUTION OF GALLIFEROUS SUBSTANCES</p>		
<p>(54) Titre: PROCEDE DE TRAITEMENT HYDROMETALLURGIQUE DE SOLUTION DE MATIERES GALLIFERES</p>		
<p>(57) Abstract</p>		
<p>A process for the hydrometallurgical treatment of a solution of galliferous substances containing in addition at least one metalloid from column V of the period classification of the elements comprises the following steps: b) adjustment of the concentration of chloride ions and of the acidity of said solution by addition of hydrochloric acid and alkaline or alkaline earth chloride; c) placing said solution in contact with an organic phase containing at least one neutral pentavalent phosphorous compound containing a phosphorous-oxygen double bond. Application to extractive metallurgy of gallium and accompanying elements.</p>		
<p>(57) Abrégé</p>		
<p>L'invention concerne un procédé de traitement hydrométallurgique de solution de matières gallifères contenant en outre au moins un métalloïde de la colonne V de la classification périodique des éléments. Elle est caractérisée par le fait que le procédé comporte les étapes suivantes: b) ajustement de la concentration en ions chlorure et de l'acidité de ladite solution par adjonction d'acide chlorhydrique et de chlorure alcalin ou alcalino-terreux; c) mise en contact de ladite solution avec une phase organique contenant au moins un composé phosphoré pentavalent neutre présentant une double liaison phosphore-oxygène. Application à la métallurgie extractive du gallium et des éléments l'accompagnant.</p>		

PROCESS FOR THE HYDROMETALLURGICAL TREATMENT OF A SOLUTION
OF MATERIALS CONTAINING GALLIUM

5 The present invention relates to the recovery of
gallium contained in various raw materials or secondary
raw materials together with impurities such as the metal-
loids of Group V of the periodic table of the elements.

10 More particularly it relates to the treatment
either of solutions of gallium chloride, or of materials
containing gallium in the wholly or partially reduced
state.

As an example of reduced materials of this kind
containing gallium may be mentioned gallium metal and the
phosphides, arsenides, nitrides and antimonides of this metal.

15 Gallium, whether present in primary or secondary
raw materials, is often combined with Group V elements:
thus, the dust from phosphorus plants, the residues from
processing of gallium arsenide and gallium phosphide and
so on.

20 For economic reasons, it is preferable that the pro-
cesses for the treatment of these products or of these solu-
tions employ techniques of the chloride route already partial-
ly perfected for the primary recovery of gallium where impuri-
ties of this kind do not occur. In general these techniques
25 employ trialkyl phosphates, particularly the most common of
these tributyl phosphate, currently designated by its letter
symbol in English TBP, which will serve as a paradigm for this
family (cf. Science and Technology of tributyl phosphate, volume
2, pages 97-99, RC Press Inc).

30 An initial difficulty lies in the presence, among
the materials containing gallium, of other elements having
similar chemical properties such as, for example, indium
and more generally metals having volatile suboxides.
Furthermore, the Group V elements often have properties
35 similar to those of III compounds, which makes separation
difficult.

According to the conventional techniques for



the recovery of gallium, this element is brought into hydrochloric acid solution and is recovered by liquid-liquid extraction of the gallium trichloride formed by means of liposoluble complexing agents of Lewis acids, agents such as amines and neutral organophosphorus compounds of the trioctylphosphine oxide (TOPO) and tributyl phosphate (TBP) type.

A second difficulty in the treatment of these secondary raw materials lies in the particularly pyrophoric and inflammable nature of these products and of the gases which they produce from their reaction with water. Thus in aqueous phases gallium phosphide produces phosphines, compounds which are very inflammable, certain of which would be the source of the combustion of natural evolutions of methane and would cause what is commonly called "will-o'-the-wisps".

It is also advisable to mention that the hydrogenous compounds of arsenic, antimony and phosphorus are highly toxic.

One of the objects of the present invention is to provide a process derived from the processes above but adapted to the particular problems of materials containing gallium mentioned above.

Thus, one of the objects of the present invention is to provide a process which enables, starting from the same extractive reactants as previously used, a good separation of gallium in the form of the chloride to be ensured from the Group V metalloids or from the impurities which are likely to be present in wastes of gallium III-V compounds or in other sources of supply of materials containing gallium. Among these impurities may be mentioned indium and antimony.

These objects as well as others which will appear subsequently are achieved by means of a process of hydro-metallurgical treatment of a solution of materials containing gallium comprising in addition at least one metalloid from Group V of the periodic table of the elements, characterized in that it comprises the following steps:

b) adjustment of the concentration of chloride ions and



the acidity of the solution to be extracted (for example obtained from step a) described below by addition of hydrochloric acid and an alkali metal chloride or an alkaline earth metal chloride;

5 c) placing the said solution in contact with an organic phase comprising at least one neutral pentavalent phosphorus compound having a phosphorus-oxygen double bond.

10 Once the gallium placed in solution at a concentration preferably at least equal to 20 g/l, advantageously from 30 to 200 g/l (the zeros not being significant figures), it is advisable to make it suitable for extraction by neutral pentavalent phosphorus compounds by controlling the level of acidity and the concentration of chloride ions so that the latter reaches a value in the
15 range 4 to 10 N, while the level of acidity must be greater than 1 N, preferably greater than 3 N, advantageously about 5 N.

20 The liquid-liquid extraction, after this adjustment, is preferably carried out with phosphorus compounds of the above type which are commercially available, such as TOPO or preferably the most common trialkylphosphate, that designated by the English acronym TBP English (tributylphosphate).

25 With the aim of better controlling the liquid-liquid extraction, both with regard to the level of viscosity and to the chemical properties, it is desirable that the trialkyl phosphate should be dissolved in aromatic hydrocarbons; in general petroleum fractions having a high boiling point and a high ignition point, such as those of
30 the type sold under the trademark Solvesso 150, are used as aromatic hydrocarbons. Generally, for economic reasons, tributyl phosphate, better known under its English acronym TBP, is used as trialkyl phosphate.

35 The organic phase preferably contains from 20 to 60%, advantageously from 30 to 50% of trialkylphosphate by volume.

In order to be selective with regard to the



impurities mentioned above, it is advisable to carry out the liquid-liquid extraction in such a way that the concentration of gallium chloride in the organic phase is at least equal to 90%, preferably to 95%, advantageously to 99% of its saturation value if it were the only extractable element.

In order to do this, adjustment is made essentially to the ratio of the organic phase to the aqueous phase limiting it as much as possible. As a guide, it will be possible to adjust the quantity of phosphorus compounds used per unit of gallium present in the solution (control of outputs). A ratio of two molecules of organophosphorus compounds per molecule of gallium chloride must be sought. It is thus preferable to be operating in the section of the extraction isotherm where this curve forms a quasi plateau. This is achieved particularly by adjusting the prescribed level of chloride and the prescribed level of acidity in step b). Thus, the ratio of the saturation value to the actual extraction value must be as close as possible to 1, hence the importance of obtaining very high gallium concentrations and, indeed, from step a) described below, equally high solids contents of the suspension, preferably in the range 50 to 500 grams per litre (to one significant figure).

Finally, to be more selective with regard to arsenic, the latter being less well extracted by the phosphorus compounds in the V form than in the III form, it is advantageous that an oxidation is carried out in such a way that at least two thirds, preferably 95%, advantageously 99% of the arsenic is present in the pentavalent form. This oxidation can be carried out at the time of the possible step a) below. This ratio, following Nernst's Law determines the redox potential of the solution. A satisfactory potential is a potential which is in the region of 1 V with reference to the Ag/AgCl electrode.

When the organic phase contains some other impurity, it is possible to wash this phase with solutions of concentrated gallium chloride. One of the best possibilities is to wash the said organic phase with an HCl-CaCl₂



mixture at the highest possible O/A ratio. The gallium chloride thus obtained can advantageously be recycled for example in the aqueous suspension phase of the possible step a) below.

5 The number of extraction stages is determined so that the extraction of gallium should be as complete as possible with as low as possible a concentration of impurities at the outlet. The number of stages is generally within the range 3 to 5.

10 Another object of the present invention is to provide an leaching process for compounds containing gallium mentioned above which gives gallium chloride and which avoids or limits the formation of toxic or inflammable gases.

15 Another aim of the present invention is to provide an aggressive process which avoids any untimely ignition of these materials containing gallium.

20 It is noteworthy that avoidance of ignition of these materials containing gallium or the gases which they generate is particularly important when these materials containing gallium comprise in addition organic diluents such as those used during processing of III-V compounds.

This object is achieved by means of the addition, before step b) of the following step:

25 a) placing gallium in solution by attacking a suspension of the said materials containing gallium with chlorine;

30 Attacking compounds of this type with chlorine is known per se but it is particularly difficult to carry out in aqueous media. It is for this reason that in a recent patent application (European Patent Application published under No. 0,219,213 filed by the company SUMITOMO METAL MINING), it has been proposed to attack compounds of this type in a bath of molten salts whose principal constituent is arsenic chloride. This has led to carrying out the separation of the arsenic chloride from gallium chloride by distillation, despite the difficulty of a technique of this type.

35 In general, when chlorine is used in the aqueous



phase to attack compounds of this type there is a high risk of explosion and particularly expensive equipment is necessary to avoid the risks of fire as well as poisoning.

5 During the study which led to the present invention it was possible to demonstrate that operating in regions, at least at the start of the reaction, where it is not usual to operate for dissolving gallium, that is at a pH where chloride is not present in solution (disproportionation > about 3) and where gallium is normally insoluble as
10 it is precipitated in the form of the trihydroxide, it was possible to avoid any ignition and any evolution of toxic materials.

15 It is preferable that the temperature of the solution during the aggressive step a) should be less than 80°C, advantageously at most equal to 50°C (these two latter values are given to a single significant figure).

20 When chlorine is mentioned, it must be understood to mean not only gaseous chlorine but also any operation capable of generating chlorine "in situ". As examples of the evolution of chlorine "in situ" may be mentioned electrolysis in a chloride medium and reactions opposite to that of the disproportionation of this halogen.

25 One of the possible embodiments of the present invention would comprise introducing chlorine in the form of hydrochloric acid and bleaching powder (mixed chloride and hypochlorite of lime one of the proposed formulae of which is CaClOCl), with the provision that the acidity limits specified above are followed.

30 One of the satisfactory ways of carrying out the reaction comprises starting with an aqueous phase having a pH within the range above (absence of dissolved chlorine and presence of precipitates of gallium hydroxide), namely a pH within the range 3 to 8, forming a pulp with the product containing gallium (step a) and bubbling chlorine
35 gas through it, then the temperature is allowed to rise under the effect of the reaction exotherm.

After step c), it is possible to carry out,



according to techniques known to practitioners of the art, a rinsing of the organic phase to eliminate particles of the aqueous phase which have been entrained in the organic phase. A washing of this type occurs in Example 4.

5 Step c) of liquid-liquid extraction can be followed, as far as the aqueous phase is concerned by a step of recovery or elimination of arsenic. These steps are known per se. As recovery step, may be mentioned a reduction of arsenic V to arsenic III followed by a distillation known
10 per se of the arsenic trichlorides. From the environmental aspects, it is also possible to precipitate the arsenic in the form of arsenate of lime and iron arsenate by adding one of these two elements in an appropriate form and adjusting the pH to the pH from precipitation of the arsenate of lime and the iron arsenate. The chloride solutions thus
15 obtained can possibly be the subject of recycling to step a) or, after evaporation and salt formation, to step b).

The organic phase loaded with gallium chloride, possibly washed as described above, can be eluted in a step
20 d) either by an aqueous phase which is lean in chloride ions (less than 1 N, preferably less than 0.1 N), or preferably reextracted by a medium containing sodium ions to form on the one hand a gallate of sodium or of another alkali metal and on the other hand sodium chloride or the chloride of another alkali metal.

25 This solution allows complete regeneration of TBP and allows in addition a step e) for recovery of gallium by electrolysis.

For this electrolysis step e), it is preferable that the concentration of free base (OH^-) is greater than
30 4 N. It is thus possible to carry out step d) of sodium carbonate elution, either by placing in contact with sodium carbonate at a quantity and in a concentration such that the residual sodium carbonate is at least equal to 0.1 N, preferably equal to 0.5 N, and subsequently
35 adjusting the quantity of base, or by placing the TBP solution in contact with a base in a quantity and a concentration such that, after the reextraction, the quantity



of residual base is at least equal to 4 N.

Thus the electrolysis step is preferably carried out with a sodium carbonate concentration at least equal to about 4 N at current densities within the range 80 (to one significant figure) and 300 (to one significant figure) A/m² and at a temperature in the range 35 to 50°C.

The examples which follow and which do not introduce any limiting characteristic are intended to enable specialists to determine readily the operating conditions which it is advisable to use in each particular case.

Example 1

100 g of gallium arsenide process sludges containing 45.5% of gallium and 47.9% of arsenic are placed in suspension in 500 ml of water. No arsine (AsH₃) is detected above the reaction vessel and no violent reaction is produced. Chlorine gas is subsequently injected into the stirred suspension at the rate of 80 g/h for 7 hours, during which the temperature rises to 75°C.

Once the attack is finished, the suspension is filtered, the residue is washed with water and 4.46 g of dry residue is recovered containing 19.4% of gallium and 0.60 l of aqueous solution containing gallium chloride. The lixiviation yield of gallium is thus greater than 98%.

Example 2

100 g of gallium phosphide process sludges, containing 56.5% of gallium and 18.5% of phosphorus, are placed in suspension in 500 ml of water. No trace of phosphines (PH₃, P₂H₄, and so on) is detected above the reaction vessel and no ignition is produced. Chlorine gas is subsequently injected into the stirred suspension at the rate of 100 g/h for 7 hours. The temperature of the suspension rises to 76°C during the reaction. When the attack is finished, the suspension is filtered, the residue is washed with water and 12.5 g of dry residue is recovered containing 0.76% of gallium and 600 ml of solution containing gallium chloride.

The lixiviation yield of gallium is thus greater than 99%.



Example 3

100 g of broken gallium phosphide wafers, previously pulverized to a granulometry of $d_{80} = 240 \mu\text{m}$, containing 71.1% of gallium and 25.7% of phosphorus are placed in suspension in 500 ml of water. No trace of phosphine (PH_3) is detected above the reaction vessel and no ignition is produced. Chlorine gas is subsequently injected into the stirred suspension at the rate of 100 g/h for 7 hours. The temperature of the suspension rises to 76°C during the reaction. When the attack is finished, the suspension is filtered, the residue is washed with water and 0.97 g of dry residue is recovered containing 33.4% of gallium and 620 ml of solution containing gallium chloride.

The dissolution yield of gallium is thus greater than 99%.

Example 4

By placing gallium in solution by using chlorine to attack a suspension of materials containing gallium defined in Examples 1, 2 and 3, and after addition of CaCl_2 , a solution PHA_{infl} is obtained whose potential relative to the Ag/AgCl electrode is about one volt and which is placed in contact, under countercurrent conditions in a battery of 4 mixer-settlers, with an organic phase formed by volume from 40% TBP and 60% SOLVESSO 150, while maintaining a ratio of organic phase to aqueous phase (O/A) of 0.9; after allowing the battery to reach chemical equilibrium, an organic phase PHO_{eff} is obtained whose composition, like that of PHA_{infl} , is given in the table below.

In a second stage, this organic phase loaded with gallium is placed in contact with an aqueous phase titrating $\text{HCl} = 1 \text{ N}$ and $\text{CaCl}_2 = 2 \text{ M}$, so as to obtain an O/A ratio of 10, under countercurrent conditions in a battery of 4 mixer-settlers. The organic phase is thus completely purified and after allowing the battery to reach chemical equilibrium an organic phase PHO_{lav} and an aqueous washing phase PHA_{lav} are obtained whose respective compositions are given in the table below.



Chemical Species	PHASES				
	PHA _{infl}	PHA _{eff}	PHO _{eff}	PHO _{Lav}	PHA _{Lav}
Ga in g/l	46.1	0.2	51.1	46.2	49.2
As in g/l	23.6	23.4	0.164	$5 \cdot 10^{-3}$	1.6
In in g/l	0.46	0.45	10×10^{-3}	$< 10^{-3}$	0.1
P in g/l	8.7	8.6			
CaCl ₂ in M	1.5	1.5			2
HCl in N	5	2.7			2
Selectivity of recovery of gallium in relation to:					
- arsenic			160	29	
- indium			51	< 9	
Cumulative selectivity:					
- arsenic				4640	
- indium				< 460	

Example 5

A solution of gallium chloride in TBP (40%) obtained by placing the latter under the conditions of the invention in contact with an industrial solution of gallium chloride is twice placed in contact with 2 N sodium carbonate at a ratio O/A = 1. The results are compiled in the table below.

The sodium carbonate consumed is equal to 1.85 N.



	Volume (l)	Ga g/l	As mg/l	In mg/l	Na g/l	Cl ⁻ g/l	Ca mg/l	OH ⁻ (N)
Initial Organic phase	4.15	37.7	44	2	-	-	-	-
Organic phase 1st contact	-	0.025	21	1	-	-	-	-
Aqueous phase 1st contact	4.4	32.5	12	1.6	30.0	61.4	15.9	0.85
Organic phase 2nd contact	4.1	0.021	17	1	-	-	-	-
Aqueous phase 2nd contact	4.3	3.2	16	2.5	19.1	35.8	35.8	1.3
Re.extraction yield %		99.9	62.0	50.0				

Example 6: Electrolysis of gallium obtained in solutions from reextraction with sodium carbonate.

Electrolysis trials were carried out starting from sodium carbonate reextraction solutions and varying as parameters the concentration of free sodium carbonate and the current density using thermal control to keep the catholyte and the anolyte at 40°C. The cathodes and anodes are of stainless steel and a recovery boat for liquid gallium is located at the lower end of the cathode.

10 During the electrolysis, the drops of gallium flow along the surface of the cathode (vertical) and are collected in the said boat. The solution containing gallium which



supplies the electrolysis tank has the following composition:

Ga = 32.5 g/l

Cl⁻ = 61.4 g/l

5 Na = 30.0 g/l

OH⁻ = 0.85 N

As = 12 mg/l

In = 1.6 mg/l

10 The parameters for the different trials are compiled in the following table:

OH ⁻ (N)	Initial concentration	Current density A/m ²	Duration (h)	Faradic yield %	Anodic phenomena
0,85	32,5	250	12	60 to 14	Evolution of Cl ₂ , formation of hypochlorites, attack
0,85	32,5	80	3	62	Evolution of Cl ₂ , attack
2	25	80	3,5	83	No dissolution appearance of some pitting
2	25	120	5	79	Slight attack
3	20	120	4,5	77	No attack, anolyte colourless
3	15	240	2,5	72	No attack anolyte slightly yellow



The gallium obtained has a purity greater than 99.99% (In and As under the limit of detection, that is less than 3 g/t and less than 8 g/t respectively).

Example 7

5 A solution of gallium chloride in TBP (Loaded organic phase obtained by placing the latter under the conditions of the invention in contact with an industrial solution of gallium chloride is placed in contact, continuously within a stirred reaction vessel, with 7 N sodium hydroxyde at a ratio O/A = 1.4. The gallium in the sodium carbonate after reextraction is analysed. The sodium carbonate consumed is equal to 2.6 N. The results are compiled in the following table:

15

Phases			
Chemical Species	Loaded organic phase	Sodium carbonate before reextraction	Sodium carbonate after reextraction
Ga in g/l	45.0		64.0
As in mg/l	15×10^{-3}		0.02
In in g/l	$< 10^{-3}$		
NaOH in N		7	

20

25

The reextraction yield of gallium is greater than 99.9%.

30



CLAIMS

1. Process of hydrometallurgical treatment of a solution of materials containing gallium comprising in addition at least one metalloid from Group V of the periodic table of the elements, characterized in that it comprises the following steps:

b) adjustment of the concentration of chloride ions and of the acidity of the said solution by addition of hydrochloric acid and an alkali metal chloride or an alkaline earth metal chloride;

c) placing the said solution in contact with an organic phase comprising at least one neutral pentavalent phosphorus compound having a phosphorus-oxygen double bond.

2. Process according to Claim 1, characterized in that step b) is carried out in such a way that the concentration of chloride ions, not counting those bonded to gallium, is within the range 4 to 10 N.

3. Process according to any one of Claims 1 and 2, characterized in that the said phosphorus compound is a trialkylphosphate.

4. Process according to Claim 3, characterized in that the said phosphorus compound is tributylphosphate.

5. Process according to any one of Claims 1 to 4, characterized in that step c) is carried out in such a way that the concentration of gallium chloride in the organic phase is equal to 90% of its saturation value if it were the only extractable element.

6. Process according to Claim 5, characterized in that the control of the concentration of gallium chloride is carried out through the ratio of organic phase to aqueous phase.

7. Process according to any one of Claims 1 to 6, characterized in that the redox potential of the solution before step b) is such that two thirds of the arsenic which may be present is in the pentavalent form.

8. Process according to any one of Claims 1 to 7,



characterized in that it comprises before step b) in addition the following step:

a) placing gallium in solution by using chlorine to attack a suspension of the said materials containing gallium;

9. Process according to Claim 8, characterized in that the temperature of the solution during the attack step a) is less than 70°C.

10. Process according to Claim 9, characterized in that the temperature of the solution during the attack step a) is at most equal to 50°C.

11. Process according to any one of Claims 8 and 9, characterized in that the said suspension of the said materials containing gallium is an aqueous suspension produced at ambient temperature.

12. Process according to Claim 11, characterized in that during step a) the temperature is allowed to rise under the effect of the reaction exotherm.

13. Process according to any one of Claims 11 and 12, characterized in that at the beginning of the attack the said suspension has a pH within the range 3 to 8.

14. Process according to any one of Claims 8 to 13, characterized in that the concentration of solids in the suspension of materials containing gallium is in the range 50 to 500 grams per litre.

15. Process according to any one of Claims 1 to 14, characterized in that it comprises in addition the following step:

d) reextraction of the said organic phase in a sodium hydroxyde medium.

16. Process according to any one of Claims 1 to 15, characterized in that it comprises in addition the following step:

e) recovery of gallium by electrolysis in an electrolyte whose concentration of free base is at least equal to 4 N.



INTERNATIONAL SEARCH REPORT

International Application No PCT/FR 88/00574

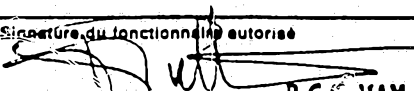
I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. ⁴ C 22 B 58/00; C 22 B 3/00; C 01 G 15/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int. Cl. ⁴	C 22 B 58/00; C 22 B 3/00; C 01 G 15/00	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	Patent Abstracts of Japan, Vol. 11, no. 53 (C-404) (2500), 19 February 1987, & JP, A, 61215214 (DAIHACHI K.K.) 25 September 1986	1
A	EP, A, 0219213 (SUMITOMO METAL MINING) 22 April 1987 see claim 1 cited in the application	
A	DE, A, 3235136 (HOECHST) 29 March 1984 see page 3	1
A	GB, A, 2184108 (ELKEM) 17 June 1987	
A	US, A, 4094753 (CHARLTON et al.) 13 June 1978	

<p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the International filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the International filing date but later than the priority date claimed</p> <p>"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
31 January 1989 (31.01.89)	28 February 1989 (28.02.89)	
International Searching Authority	Signature of Authorized Officer	
European Patent Office		

RAPPORT DE RECHERCHE INTERNATIONALE

Demande internationale N°

PCT/FR 88/00574

I. CLASSEMENT DE L'INVENTION (si plusieurs symboles de classification sont applicables, les indiquer tous) ⁷		
Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB		
CIB ⁴ : C 22 B 58/00; C 22 B 3/00; C 01 G 15/00		
II. DOMAINES SUR LESQUELS LA RECHERCHE A PORTÉ		
Documentation minimale consultée ⁸		
Système de classification	Symboles de classification	
CIB ⁴	C 22 B 58/00; C 22 B 3/00; C 01 G 15/00	
Documentation consultée autre que la documentation minimale dans la mesure où de tels documents font partie des domaines sur lesquels la recherche a porté ⁹		
III. DOCUMENTS CONSIDÉRÉS COMME PERTINENTS ¹⁰		
Catégorie [*]	Identification des documents cités, ¹¹ avec indication, si nécessaire, des passages pertinents ¹²	N° des revendications visées ¹³
A	Patent Abstracts of Japan, volume 11, no. 53 (C-404)(2500), 19 février 1987, & JP, A, 61215214 (DAIHACHI K.K.) 25 septembre 1986 --	1
A	EP, A, 0219213 (SUMITOMO METAL MINING) 22 avril 1987 voir revendication 1 cité dans la demande --	
A	DE, A, 3235136 (HOECHST) 29 mars 1984 voir page 3 --	1
A	GB, A, 2184108 (ELKEM) 17 juin 1987 --	
A	US, A, 4094753 (CHARLTON et al.) 13 juin 1978 -----	
<p>[*] Catégories spéciales de documents cités: ¹¹</p> <p>« A » document définissant l'état général de la technique, non considéré comme particulièrement pertinent</p> <p>« E » document antérieur, mais publié à la date de dépôt international ou après cette date</p> <p>« L » document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre citation ou pour une raison spéciale (telle qu'indiquée)</p> <p>« O » document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens</p> <p>« P » document publié avant la date de dépôt international, mais postérieurement à la date de priorité revendiquée</p> <p>« T » document ultérieur publié postérieurement à la date de dépôt international ou à la date de priorité et n'appartenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention</p> <p>« X » document particulièrement pertinent: l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive</p> <p>« Y » document particulièrement pertinent: l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier.</p> <p>« A » document qui fait partie de la même famille de brevets</p>		
IV. CERTIFICATION		
Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale	
31 janvier 1989	28 FEB 1989	
Administration chargée de la recherche internationale OFFICE EUROPEEN DES BREVETS	Signature du fonctionnaire autorisé  P.C.G. VAN DER PUTTEN	