

FORM 1

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

600464

APPLICATION FOR A STANDARD PATENT

I\We,

COMPAGNIE FRANCAISE DE MOKTA

of

41 BIS, AVENUE DE L'EUROPE
B.P. 106
78143 VELIZY VILLACOUBLAY
FRANCE

hereby apply for the grant of a standard patent for an
invention entitled:

PROCESS FOR THE SEPARATION OF MOLYBDENUM
USING LIQUID-LIQUID EXTRACTION

which is described in the accompanying complete specification

Details of basic application(s):

Number of basic application	Name of Convention country in which basic application was filed	Date of basic application
86-00.994	FR	23 JAN 86

My/our address for service is care of CLEMENT HACK & CO., Patent
Attorneys, 601 St. Kilda Road, Melbourne 3004, Victoria,
Australia.

DATED this 21st day of January 1987

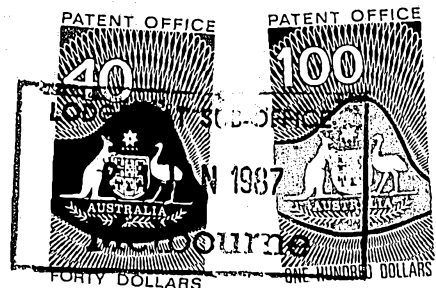
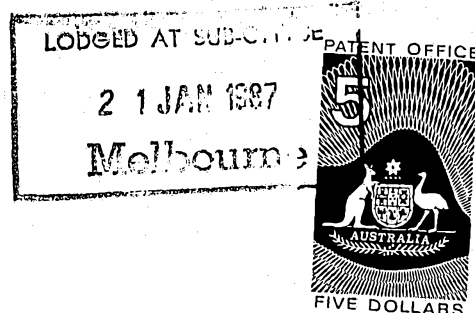
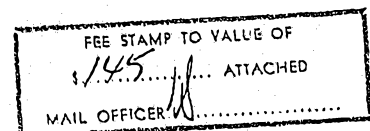
COMPAGNIE FRANCAISE DE MOKTA

CLEMENT HACK & CO.

TO: The Commissioner of Patents.

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 2.6.90



Forms 7 and 8

AUSTRALIA

Patents Act 1952

**DECLARATION IN SUPPORT OF A CONVENTION OR NON-CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION**

Name(s) of
Applicant(s)

In support of the application made by COMPAGNIE FRANCAISE DE MOKTA

Title

for a patent for an invention entitled PROCESS FOR THE SEPARATION OF
MOLYBDENUM BY LIQUID-LIQUID EXTRACTION

Name(s) and
address(es)
of person(s)
making
declaration

I/We, Jean Moine, General Manager of COMPAGNIE FRANCAISE DE
MOKTA, 41 bis, avenue de l'Europe B.P. 69 78143 VELIZY-
VILLACOUBLAY (FRANCE)

do solemnly and sincerely declare as follows:—

1. I am/we are the applicant(s) for the patent, or authorised by the abovementioned applicant to make this declaration on its behalf.
2. 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) namely:—

Country, filing
date and name
of Applicant
for the or
each basic
application

in FRANCE on January 23, 19 86
by COMPAGNIE FRANCAISE DE MOKTA
in _____ on _____ 19 _____
by _____

3. The said basic application(s) was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.
4. The actual inventor(s) of the said invention is/are

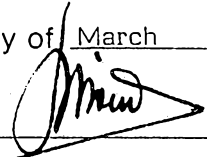
Name(s) and
address(es)
of the or each
actual inventor

Didier BEUTIER, 48, boulevard Edgar Quinet 75014 PARIS
Yves LE QUESNE, 35, rue Mathurin Regnier 75015 PARIS

5. The facts upon which the applicant(s) is/are entitled to make this application are as follows:—
"The applicant would be entitled to have assigned to it a patent
granted to any of the actual inventors in respect of the said
invention".

See reverse
side of this
form for
guidance in
completing
this part

DECLARED at Vélizy this 19th day of March 1990


President Directeur Général

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MOLYBDENUM FROM URANIUM SOLUTIONS WITH 8-HYDROXYQUINOLINE
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- (71) Applicant(s)
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GRIFFITH HACK & CO. _MELBOURNE
- (56) Prior Art Documents
AU 74247/81 B01D 11/04
AU 519020 42539/78 B01D 11/04
AU 448131 57173/69 B01D 11/04; 28.8
- (57) Claim

1. A process for the selective removal of molybdenum present in a sulfuric solution containing uranium in addition to molybdenum, comprising:

 a) contacting said sulfuric solution with an organic liquid phase containing, as extractant, at least one compound having a 7-20 carbon atoms substituted 8-hydroxyquinoline as an active agent to selectively extract said molybdenum into said organic liquid phase, and

 b) reextracting said organic liquid phase bearing said molybdenum with an alkaline aqueous solution to reextract said molybdenum into said alkaline aqueous phase.

6. The process as claimed in any of claims 1 to 5, wherein the volume relationship between the organic phases and the aqueous phases is such that there are at least four 8-hydroxyquinoline groups per atom of extractable molybdenum.

AUSTRALIA
PATENTS ACT 1952
COMPLETE SPECIFICATION

600464

Form 10

(ORIGINAL)

FOR OFFICE USE

Short Title:

Int. Cl:

Application Number:

Lodged:

Complete Specification-Lodged:

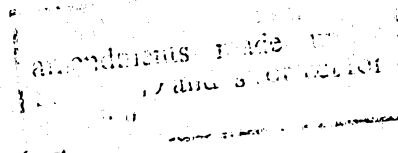
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Related Art:



TO BE COMPLETED BY APPLICANT

Name of Applicant:

COMPAGNIE FRANCAISE DE MOKTA

Address of Applicant: 41 BIS AVENUE DE L'EUROPE

B.P. 106

78143 VELIZY VILLACOUBLAY

FRANCE

Actual Inventor:

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601 St. Kilda Road,
Melbourne, Victoria 3004,
Australia.

Complete Specification for the invention entitled:
PROCESS FOR THE SEPARATION OF MOLYBDENUM
USING LIQUID-LIQUID EXTRACTION

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

The present invention relates to a process for the
5 separation of molybdenum present in sulfuric solutions. It
relates more particularly to a method for the extraction of
molybdenum which is selective with respect to uranium, and
where appropriate, with respect to amphoteric elements such as
arsenic, vanadium and the like.

10 In most processes for recovering uranium from its
ores, the said ore is leached with sulfuric acid in the
presence, if appropriate, of an oxidizing agent such as
hydrogen peroxide or chlorates, in order to oxidize all the
uranium IV to uranium VI. The leachate thus produced is
15 subjected to a liquid-liquid extraction or to an extraction
using resin, which involves amino groups. During this
extraction, the molybdenum is extracted together with uranium.

The very high affinity of molybdenum for the amine makes it extremely difficult to reextract, with the result that molybdenum accumulates in the solvents or in the resins and this, on the one hand, reduces the capacity of the solvents and, on the other hand, causes scums to form at the interfaces between the solvent and the reextraction solution. The only way to remove the molybdenum consists of a complete regeneration of the solvent in a basic medium; this regeneration is both costly in reactants and leads to losses of uranium. Furthermore, when the molybdenum is at a high concentration in the aqueous phase, this also applies to the organic phase, and results in it being partially eluted when the reextraction is carried out. This elution leads to contamination of the uranium and to a major loss of its commercial value.

Thus, molybdenum, which is almost always associated with uranium, represents a considerable inconvenience in the processes for upgrading this metal. In some cases, the concentration of molybdenum is so high that the upgrading of this metal may be economically profitable. The value at stake is sufficiently high for numerous studies to have been carried out and for numerous processes to have been proposed to avoid this problem.

A first group of processes which have been proposed consists in extracting uranium and molybdenum with an amino solvent and then performing a reextraction using an acidic solution of an alkali metal or alkaline-earth metal chloride in the presence of an oxidizing agent. This stage is then followed by a reextraction of the residual molybdenum using alkali metal carbonate. A process of this kind, described in the article of the ISEC, Toronto, September 77 (B. Scalino et al) and in French Patent 2,484,989, while making it possible to overcome the scum formation and to improve the separation of uranium from molybdenum, does not do away with either the need for a regeneration of the solvent or a high usage of costly reactants (oxidizing agent and alkali metal carbonate).

Furthermore, it does not permit molybdenum to be upgraded and increases the usage of extractant, since it is known that amines are highly sensitive to oxidation.

Another group of processes, such as that described
5 in French Patent 2,451,891, tries to solve the problem by extracting molybdenum using an extractant of the same type as the extractant for uranium, namely a secondary or tertiary amine. This solution is, on the one hand, costly, since in each extraction cycle it requires a complete regeneration of
10 the molybdenum-bearing amine in order to recover this metal effectively therefrom and, on the other hand, it is very laborious when the concentration of molybdenum are low.

Lastly, a third group of processes proposes a selective extraction of molybdenum using an anion exchange
15 resin or activated charcoal, prior to the extraction of uranium. Processes of this kind are described, for example, in the publication IEA, Volume 292, 1973 (H.T. Matsuda et al) and in French Patents 2,414,478 and 2,531,060. The proposed anionic resins are weak resins in which the groups are
20 secondary or tertiary amines. However, although they are selective with respect to uranium, these resins are not sufficiently selective, and this means either that a proportion of uranium is fixed on the resin and greatly complicates the uranium recovery circuits, or that molybdenum
25 is incompletely fixed and continues to interfere with the liquid-liquid extraction. It is difficult, furthermore, to obtain a total elution.

With regard to the fixation of molybdenum on activated charcoal, fixation tests show good capacities (a
30 capacity of 90 grams per liter in the case of a solution containing 0.42 grams per liter). However, a process of this kind is, on the one hand, relatively unsuitable for high flow rates and, on the other hand, does not solve the problem of the remaining impurities, and this makes it very difficult to
35 upgrade the molybdenum present in the medium.

Taking all the abovementioned into account, the purpose of the present invention is to find a process capable of selectively fixing molybdenum with respect to uranium and, if appropriate, iron, arsenic, phosphorus, silicon and 5 vanadium.

Another purpose of the present invention is to find a process of the abovementioned type which permits molybdenum to be readily recovered, and the extractants used to be readily regenerated.

10 These purposes and others which will appear hereinafter are achieved by means of a process for the separation of molybdenum present in a sulfuric solution, in which:

 (a) the said sulfuric solution is placed in contact with 15 an organic liquid phase containing, as extractant, at least one compound containing 8-hydroxyquinoline (generally known as oxine) as an active group;

 (b) the said molybdenum-bearing phase is reextracted using an alkaline aqueous solution.

20 The elution stage (b) is preferably performed using a solution whose pH is greater than 10. As eluent solution there may be chosen alkali metal salt of ammonium hydroxides and carbonates of these same cations.

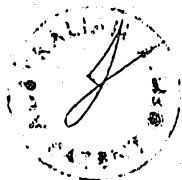
 Solutions of alkali metal hydroxides whose 25 concentration is between 0.1 N and the solubility limit will preferably be chosen. A good compromise consists in choosing a concentration of between 0.5 and 2 N. Since sodium hydroxide is one of the least expensive bases, it may be satisfactory to choose this alkali metal hydroxide.

30 In so far as the fixation stage (a) is concerned, it is advantageous to fix the pH of the sulfuric solution at a value of less than 2, preferably less than 1. However, for reasons of economy, it is difficult to acidify this solution excessively, unless it is recycled into the process.

In order to produce an eluate which is as pure as possible with respect to molybdenum, it may be desirable to precede stage (b) by a washing of the organic phase using a sulfuric solution whose concentration is greater than 1 M.

5 The stages (a) and (b), and the optional washing stage, are preferably carried out at a temperature between ambient temperature and 60°C and at atmospheric pressure in order to avoid interface scums. The volume relationship between the organic phase and the aqueous phases should be
10 such that there are at least four 8-hydroxyquinoline groups per atom of extractable molybdenum. The molecule containing an active 8-hydroxyquinoline group is preferably an 8-hydroxyquinoline substituted in the 7 position by a saturated or unsaturated aliphatic chain containing 7 to 20
15 carbon atoms. As satisfactory molecules there may be mentioned the products sold under the trade name Kelex 100 (cf. G.P. Demopoulous and P.A. Distin, Hydrometallurgy, 11, 389-396).

Water-immiscible polar solvents can be used to
20 obtain satisfactory dissolution of the polar molecules formed by the substituted 8-hydroxyquinolines. However, a large majority of these solvents (trichloroethylene, chloroform, ether, ester etc) present disadvantages in use, which are connected either with their instability, or their toxicity, or
25 lastly with their flammability. This is why, in addition to reasons of an economic nature, it frequently appears desirable to use heavy oil fractions mixed with a polar solvent (at a concentration of preferably 50% and 5 to 30% by volume), such as long-chain (C₈ to C₁₆) alcohols, phosphorus compounds
30 (alkyl phosphate, phosphonate or phosphinate, trialkylphosphine oxide), sulfur compounds (sulfone or sulfoxide) and, generally, polar ^{Lipophilic}~~lipophilic~~ compounds. Mixtures which offer the best compromise between efficiency and cost of manufacture are Kelex 100 5 to 30% by volume - heavy alcohol 5 to 30%,
35 Solvesso 150 q.s. 100%, that is to say an oil fraction



containing a high percentage of aromatic compounds. To avoid any interface scums, the oil fraction must contain at least 50% of aromatics.

The eluate containing molybdenum is advantageously acidified to a pH which makes it possible, after addition of an alkaline-earth metal salt, to precipitate the molybdenum in the form of the alkaline-earth metal molybdate.

The following examples, which do not imply any limitation, enable the specialist to better apprehend the various parameters of the process according to the invention.

Example 1: Effect of the composition of the extractant phase.

An organic phase consisting (on a volume and percentage basis) of 20% of Kelex 100, 10% of tridecanol, 70% of aromatic diluent, is placed in contact with an aqueous phase containing molybdenum, introducing a quantity of molybdenum which is less than a quarter of the molarity of Kelex in the organic phase (0.58 M).

When Solvesso 150, ^{an aromatic chain diluent} is used, no precipitation takes place; when Kscaid 100 (an aliphatic chain diluent containing 25% of aromatics by weight) is used, a significant proportion of the extracted molybdenum precipitates in the form of a sludge at the interface.

All the examples which follow will therefore be conducted with the use of the mixture based on Solvesso 150.

Example 2: Extraction of molybdenum

(a) initial aqueous phase: 1.8 grams per liter of molybdenum, 15 grams per liter of sulfuric acid - pH = 1. At various organic phase/aqueous phase ratios (0.2 - 0.5 - 1 - 2 - 4), at a temperature of 20°C and after 15 minutes, all the molybdenum is fixed in the solvent. At equilibrium, there is a concentration of molybdenum in the aqueous phase of less than one milligram per liter and a concentration of molybdenum



in the organic phase which is equal to 9 - 3.6 - 1.8 - 0.9 and 0.45 grams per liter, respectively, according to the abovementioned organic phase/aqueous phase ratios.

(b) Initial aqueous phase: 5.1 grams per liter of molybdenum, 15 grams per liter of sulfuric acid. At organic phase/aqueous phase ratios of 0.2 - 0.3 - 0.4 and 0.5, the molybdenum disappears from the aqueous phase (concentration below one milligram per liter) in all cases. At ratios of 0.2 and 0.3, a precipitate and sludges form at the organic phase/aqueous phase interface, corresponding to maximum fixations of 25.5 and 17 grams per liter, respectively. At organic phase/aqueous phase ratios of 0.4 and 0.5, no precipitate is observed and the concentration of molybdenum in the organic phase is equal to 12.75 and 10.2 grams per liter, respectively.

The molybdenum is thus completely extracted from the aqueous phase. However, it has a solubility limit in the aqueous phase which lies between 12.75 grams per liter (i.e. 0.133 mole per liter), at which no precipitation takes place, and 17.0 grams per liter (i.e. 0.177 mole per liter), at which a precipitation is observed. Now, there is 0.58 mole per liter of chelating function; the fixation of the molybdenum therefore takes place in a proportion of one molecule of molybdenum per 3.3 to 4.4 molecules of chelating function.

The extraction coefficient of molybdenum is equal to at least 12.75×10^3 , i.e. 12,750 (ratio of the concentrations at equilibrium).

Example 3: Extraction of uranium

The initial aqueous phase contains 5.7 grams per liter of uranium and 15 grams per liter of sulfuric acid. After various contacts with the organic phase, at variable organic phase/aqueous phase ratios, the uranium remains in aqueous solution. The concentration of uranium in the organic phase is at most equal to 0.1 gram per liter. the extraction coefficient of uranium is thus less than 0.1/5.7, i.e. less than 0.02.

Example 4: Extraction of iron

The initial aqueous phase contains 7.3 grams per liter of iron and 15 grams per liter of sulfuric acid. The following results are obtained at the various organic phase/aqueous phase ratios tested:

Organic phase/aqueous phase ratio		0.2	1	2	4
10	Concentration of iron in the aqueous phase (g/l)	7.1	6.3	5.8	5.7
15	Concentration of iron in the organic phase (g/l)	1	1	0.75	0.4

The maximum concentration of iron in the solvent is thus one gram of iron per liter (i.e. 0.018 mole per liter) and the extraction coefficient of iron is at most equal to $1/0.3$, i.e. 0.16.

20 Example 5: Extraction in a uranium + molybdenum + iron medium

The initial aqueous phase contains 5.7 grams per liter of uranium, 7.2 grams per liter of iron, 1.7 grams per liter of molybdenum and 15 grams per liter of sulfuric acid. 25 After 15 minutes' contact, at various organic phase;aqueous phase ratios, the following results are obtained:

Organic phase/ aqueous phase	0.5	1	2
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5 Aqueous phase

U concentration	5.7 g/l	5.7 g/l	5.7 g/l
Fe concentration	6.8 g/l	6.6 g/l	6.5 g/l
Mo concentration	<10 mg/l	<10 mg/l	<10 mg/l

10 Organic phase

U concentration	0 g/l	0 g/l	0 g/l
Fe concentration	0.8 g/l	0.6 g/l	0.35 g/l
Mo concentration	3.4 g/l	1.7 g/l	0.85 g/l

- 15 The solvent extracts molybdenum completely, iron slightly and uranium not at all. It is thus extremely selective for molybdenum with respect to uranium and iron.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the selective removal of molybdenum present in a sulfuric solution containing uranium in addition to molybdenum, comprising:
 - a) contacting said sulfuric solution with an organic liquid phase containing, as extractant, at least one compound having a 7-20 carbon atoms substituted 8-hydroxyquinoline as an active agent to selectively extract said molybdenum into said organic liquid phase, and
 - b) reextracting said organic liquid phase bearing said molybdenum with an alkaline aqueous solution to reextract said molybdenum into said alkaline aqueous phase.
2. The process as claimed in claim 1, wherein said sulfuric solution further contains at least one of iron, arsenic, phosphorus, silicon and vanadium.
3. The process as claimed in claim 1 or 2, wherein in the contacting stage a), the sulfuric solution has a pH value of less than 2.
4. The process as claimed in any of claims 1 to 3, wherein the stage b) is preceded by a stage of washing the organic phase using a sulfuric solution of a concentration which is greater than 1 M.
5. The process as claimed in any of claims 1 to 4, wherein the stages a) and b) are conducted at a temperature between ambient temperature and 60 degrees C and at atmospheric pressure.
6. The process as claimed in any of claims 1 to 5, wherein the volume relationship between the organic phases and the aqueous phases is such that there are at least four 8-hydroxyquinoline groups per atom of extractable molybdenum.

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7. The process as claimed in any of claims 1 to 6, wherein the organic liquid phase comprises a solvent selected from the group consisting of a polar lipophilic compound and a heavy oil fraction.

8. The process as claimed in any of claims 1 to 7, where the alkaline aqueous solution in stage b) is a solution of a hydroxide of an alkali metal whose concentration is between 0.1 M and the solubility limit.

DATED THIS 21ST DAY OF FEBRUARY, 1990.

COMPAGNIE FRANCAISE DE MOKTA
By Its Patent Attorneys:

GRIFFITH HACK & CO.
Fellows Institute of Patent
Attorneys of Australia.

