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(54) **Electrolytic process for the manufacture of salts.**

(57) A process for manufacturing a metal salt comprises passing an electric current through an electrolytic cell comprising an anode formed from or containing the metal, a cathode, an anolyte which will provide the anions to form the salt and a catholyte, the anode and the cathode being separated by a microporous plastics separator which has a pore size in the range of from 0.01 to 10 microns and a pore volume in the range of from 45 to 55%. The process may be carried out continuously or semi-continuously.

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ELECTROLYTIC PROCESS FOR THE MANUFACTURE OF SALTS

The present invention relates to an electrolytic process for the manufacture of salts.

The production of salts. i.e. the chemical compounds formed by metal ions and acid/alkali anions, can be carried out in many ways. Traditionally the simplest routes have been selected, for example those metals which are readily and easily attacked by the acids or alkalis to form salts are well known,

e.g. $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$

For metals which are not readily attacked by the particular acids then synthetic routes via metal containing compounds are preferred,

e.g. $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$

It will be appreciated however, that the use of a compound containing a metal for salt formation is always more expensive than the use of the metal itself and a direct route is therefore economically preferable. However, in many cases the direct route is not thermodynamically favoured and aggresive reaction conditions such as high temperatures and pressures and long reaction times are often required. These processes become expensive in energy, time and capital costs.

We have now developed an economic electrolytic process for the manufacture of salts in which the energy involved is mainly that of an anodic corrosion process.

Accordingly, the present invention provides a process for the manufacture of a metal salt, which process comprises passing an electric current through an electrolytic cell comprising an anode formed from

or containing the said metal, a cathode, an anolyte which will provide the anions to form the salt and a catholyte, the anode and the cathode being separated by a microporous plastics separator which has a pore size in the range of from 0.01 to 10 microns and a pore volume in the range of from 45 to 55%.

In the process of the present invention, the metal which forms the anode loses electrons to give metal ions, e.g. M^{2+} by one reaction

$$M - 2e \longrightarrow M^{2+}$$

These ions exist either as totally ionised metal ions together with the corresponding anions A^{2-}, or in an equlibrium

$$MA \rightleftharpoons M^{2+} + A^{2-}$$

The position of this equilibrium depends upon the temperature, metal ion concentration, pH etc.

The anode may comprise one of the following:

a) an ingot of the metal whose salt is to be produced,

b) granulated metal or scrap pieces of the metal whose salt is to be produced contained in a conductive basket or an insulated basket with an appropriate current feed,

c) a non-soluble anode when the process is used to change the valency state of a metal ion and thus the nature of the salt which constitutes the anolyte, and

d) granulated or particulate samples of mixed metals where metal separation and salt production are required.

The cathode used in the process of the present invention remains inert and since in general some of the metal will pass through the separator and coat the cathode it is preferred to use a cathode of the metal concerned, although a cathode of another metal may

also be used.

A cathodic reaction takes place at the cathode, for example the production of hydrogen by the reduction of the acid cation:

$$2H^+ + 2e \longrightarrow H_2$$

When hydrogen is produced during the reaction then it is necessary to ventilate the cell, or to remove the hydrogen in some other manner, in order to avoid the build-up of hydrogen and the associated danger of explosion.

Other cathodic reactions can also be carried out.

The anolyte is an electrolyte which contains ions that will conduct electricity, which provides the anions so as to form the metal salt, and in which the metal salt produced in the process of the invention is reasonably soluble. The anolyte may be an acid, such as sulphuric acid, hydrochloric acid, nitric acid, acetic acid, or an alkali, such as sodium or potassium hydroxide, or ammonium hydroxide.

The catholyte may comprise any electrolyte, but the preferred catholyte is an electrolyte which is the same as the anolyte, but not necessarily at the same concentration.

The process of the present invention is suitable for the production of many metal salts and, in particular, salts of cobalt, nickel and tin. Specific examples of salts which may be prepared by the process of the invention are stannous sulphate, silver nitrate, copper acetate, cobalt chloride, cobalt acetate and manganese acetate.

The temperature, concentration and current density employed in the process of the invention depend upon the reaction which is being carried out.

The microporous plastics separator used in the process of the present invention preferably has a pore

size in the range of from 0.01 to 0.1 microns and a pore volume of about 50%. The porosity or pore volumne controls the electrical resistance of the separator, whilst the pore size influences the transport of ions across the separator. The microporous plastics separator should be chemically resistant to its environment at the operating temperature and the operating pH. It should also be made from a plastics material which is wettable, or which can be treated to render it wettable, and possesses sufficient mechanical strength so that it is capable of being engineered into an appropriate support. It must be capable of transporting ions under an electrical and/or concentration gradient and it must also permit a reasonably high current density e.g. 50mA/cm^2 of separator surface. Examples of the microporous plastics separator are a filled polyethylene separator sold under the Trade Name DARAMIC (W.R. Grace & Co.), an irradiated polyethylene separator sold by Raychem, a microporous polyolefin manufactured by Schumacher, a compound called GORTEX which is a microporous polytetrafluoroethylene and a product called VYON/PORVAIR which is a microporous high density polyethylene. The separator is usually fabricated onto a support frame, for example by means of an adhesive or by thermal or ultrasonic welding. Such a frame enables the separator to be mounted in a cell and provides some support to the separator against bulging which is particularly important for those materials which expand when wet and bulge.

It will be understood that any two or three compartment cell may be used in the present invention. However, it is generally more convenient to design a cell having the anode, cathode and separator planar to the walls of the vessel in which they are placed. Similar considerations apply when

using a granular anode since the baskets in which the material is held are usually planar and rectangular baskets are easier to handle than circular ones. The cell should preferably have a symmetrical design so that the anode is attacked from both sides at an equal rate. The electrodes may be suspended in the cell from appropriate hooks e.g. of titanium, from lugs cast onto the electrode or by bolting the electrodes onto an appropriate bus bar.

The process of the present invention may be a continuous or a batch process. For continuous operation some pumping of the electrolytes will be required but it is preferable to use external pumps so as not to interfere with the cell symmetry. Similarly if heating is required it is preferred that it is either external or that electrically controlled heating elements are positioned at the sides of the anode and cathode compartments of the cell.

Stirring is often beneficial in order to even the rate of corrosion of the anode. Gas stirring is preferred as it leaves the cell uncluttered and is easily controlled.

The volume of the anolyte depends mainly upon the throughput required and thus is generally related to the product requirement, the stability of the product and the size of any ancillary equipment used for working up and extracting the product.

The volume of the catholyte is preferably the same as that of the anolyte since it is preferred to use the catholyte to replace the anolyte on completion of the reaction.

In order to optimise the economics of the cell the anode area should be as large as possible, providing that the available area of microporous plastics separator can pass the current required having regard to the optimum current density required for the

process. The cathode area is preferably chosen to be one of two extremes. Either the surface area is large and the current density is kept low so that any metal ions penetrating to the cathode compartment are electrodeposited onto the cathode, or the surfaces are small and the current density is kept high and hydrogen evolution prevents much of the metal being deposited on the cathode.

It is also possible to carry out the process of the present invention in a filter press type cell in which each segment of the cell is separated from the next segment of the cell by means of a separator as hereinbefore described. Alternate pairs of separators provide the anode compartment and cathode compartment, respectively. A filter press type cell is particularly useful for carrying out the process of the invention in a continuous manner. It is possible to alter the rate of flow through the cell and the current density so that a solution of the metal salt is produced which has an appropriate concentration of the metal salt therein. The metal salt solution produced may in some instances be used without further processing in a conventional chemical process. Carrying out the process of the present invention continuously using a filter press type cell is advantageous if a relatively unstable metal salt is produced since the process time is minimized and this helps to avoid disintegration of the unstable salt.

When a granular anode is used in the process of the invention it is preferred for the separator to surround the anode basket. In this arrangement the cell does not have separate compartments. The volume of anolyte required is thus considerably reduced since it is equal to the volume of the basket surrounded by the separator minus the volume of the granulated metal. The anolyte is pumped into and out of each

anode basket surrounded by separator, for example by means of a pipe which extends into the basket. It is thus possible using this arrangment for the metal salt solution to be removed from the cell at regular intervals, i.e. in a semi-continuous manner.

The process of the present invention will be further described with reference to the accompanying Figure which shows a cell in which the reaction may be carried out.

Referring to the drawing, anodes 1 are placed in the central compartment 6 of a five compartment cell. The anodes are hung from the anode rail 2. On either side of the anode compartment 6 are middle compartments 6 which do not contain any electrodes. The middle compartments 8 are separated from the anode compartment by separators 5 of a microporous plastics material. On either side of the middle compartments 8 are cathode compartments 7 which are separated from the middle compartments by separators 5 of a microporous plastics material. The cathode compartments 7 contain cathodes 3 which are suspended from cathode rails 4. The compartments 6, 7 and 8 are filled with the appropriate electrolyte and the current switched on and adjusted to the required current density.

As the reaction proceeds the metal ion concentration in compartment 6 builds up and as the anodes 1 corrode they are replaced by fresh anodes. The anodes are preferably replaced in sequence as this permits a realistic amount of the anode area to be used and hence a reasonable current density to be used. If an appreciable amount of the metal, say 7 to 10%, has been coated onto the cathode, then the cathode may be hung on the anode rail to function as an anode until the coating has redissolved.

When the metal salt produced in compartment 6

reaches a level where extraction is viable, the anodes are removed from the compartment, the anolyte pumped out of the cell and the anolyte replaced either by fresh electrolyte which is generally the electrolyte from compartments 7 or 8, if necessary augmented with further chemicals.

The anodes in compartment 6 are replaced, all of the compartments 6, 7, and 8 are topped up with electrolyte, as necessary, and the cell switched on for the process to recommence.

The present invention will be further described with reference to the following Examples.

Example 1

Production of Stannous Sulphate

A tin anode was dissolved in 2N sulphuric acid in a two compartment cell having a microporous polyethylene separator separating the anode and cathode compartments which both had a volume of 2.5L (total cell volume 5L). The cell was operated under the following conditions:

Anode Current Density	15 mA/cm^2
Cathode Current Density	60 mA/cm^2
Temperature	Ambient
Initial Sulphuric Acid Concentration	2N
Final Concentration of Tin as Stannous ion	100 g/l
Weight loss of Tin Anode	270.5g
Anode Current efficiency	98%
Metal Transfer to Catholyte	15 g

Example 2

Production of Stannous Sulphate

A tin anode was dissolved in 2N sulphuric acid in a two compartment cell having a filled microporous polyethylene separator separating the anode and cathode compartments. The cell had a total volume of 20L (7L anolyte and 13L catholyte). The cell was operated under the following conditions:

Anode Current Density	15 mA/cm^2
Cathode Current Density	15 mA/cm^2
Temperature	Ambient
Initial Sulphuric Acid Concentration	2N
Final Concentration of Tin as Stannous ion	160 g/l
Weight loss of Tin Anode	1150 g
Anode Current efficiency	98%
Metal Transfer to Catholyte	30 g
Final Sulphuric Acid Concentration	0.1 N

Example 3

Production of Silver Nitrate

A silver anode was dissolved in 1N nitric acid in a three compartment cell having a filled microporous polyethylene separators separating the compartments thereof. The anode and cathode compartments of the cell both had volumes of 0.5L. The cell was operated under the following conditions:

Anode Current Density	40 mA/cm^2
Cathode Current Density	10 mA/cm^2
Temperature	Ambient
Initial Nitric Acid Concentration	1N
Final Concentration of Silver in Anolyte	40 g/l
Weight loss of Silver Anode	21 g
Anode Current efficiency	98%
Final Concentration of free Nitric acid	0.52 N

Example 4

Production of Cobalt Chloride

Cobalt chips were placed in a titanium anode basket in 5N hydrochloric acid in a two compartment cell having a filled microporous polyethylene separator separating the anode and cathode compartments which both had a volume of 1.0L (total cell volume 2L). The cell was operated under the following conditions:

Anode Current Density	30 mA/cm^2
Cathode Current Density	20 mA/cm^2
Temperature	35°C
Initial Sulphuric Acid Concentration	5N
Final Concentration of Cobalt in the Anolyte	192.3 g/l
Weight loss of Cobalt Anode	196 g
Anode Current efficiency	98%
Metal transfer to Catholyte	2.5 g

Example 5

Production of Copper Acetate

A copper anode was dissolved in 2N acetic acid in a two compartment cell having a filled microporous polyethylene separator separating the anode and cathode compartments which both had a volume of 0.5L (total cell volume 1L). The cell was operated under the following conditions:

Anode Current Density	20 mA/cm^2
Cathode Current Density	20 mA/cm^2
Temperature	10°C
Initial Acetic Acid Concentration	2N
Final Concentration of Copper in the anolyte	41 g/l

Example 6

Production of Gold Chloride

A gold anode was dissolved in 5N hydrochloric acid in a three compartment cell having a filling microporous polyethylene separator separating the cell compartments which all had a volume of 0.2L (total cell volume 0.6L). The cell was operated under the following conditions:

Anode Current Density	40 mA/cm^2
Cathode Current Density	20 mA/cm^2
Temperature	60°C
Initial Hydrochloric Acid Concentration	5N
Final Concentration of Gold in the anolyte	50 g/l
Weight loss of Gold Anode	10.2 g
Anode Current effeciency	98%

Example 7

Production of Cuprammonium Salt

A copper anode was dissolved in a mixture of 4M ammonium hydroxide and 1M ammonium nitrate in a two compartment cell having a polyethylene separator sold under the Trade Name DARAMIC separating the anode and cathode compartments. The cell was operated under the following conditions:

Anode Current Density	25mA/cm^2
Temperature	25^{o}C
Initial pH of anolyte	pH 10
Concentration of copper as cupric ion in anolyte	33 g/l
Anode Current Efficiency	98%

The above run was repeated under the same conditions using a microporous polytetrafluoroethylene separator which had been rendered wettable by immersion in methanol for about 1 hour. Similar results were obtained.

Example 8

Production of Copper Pyrophosphate.

A copper anode was dissolved in a mixture of 2M sodium pyrophosphate, 0.5M sodium nitrate and 0.1M ammonium hydroxide in a two compartment cell having a filled microporous polyethylene separator separating the anode and cathode compartments. The cell was operated under the following conditions:

Anode Current Density	$5mA/cm^2$
Temperature	25^oC
Initial pH of anolyte	pH 10
Concentration of copper as cupric ion in anolyte	25 g/l
Anode Current Efficiency	99%

The above run was repeated under the same conditions using a microporous polytetrafluoroethylene separator sold under the name GORTEX which had been rendered wettable by immersion in methanol for about 1 hour. Similar results were obtained.

Example 9

Production of Sodium (or Potassium) Stannate.

A tin anode was dissolved in 3N sodium or potassium hydroxide in a two compartment cell having a microporous polytetrafluoroethylene separator sold under the name of GORTEX separating the anode and cathode compartments. The separator had previously been rendered wettable by immersion in methanol for about 1 hour. The cell was operated under the following conditions:

Final Anode Current Density	20mA/cm^2
Temperature	60-90^{o}C
Initial pH of anolyte	13
Concentration of tin as stannous ion in anolyte	55 g/l
Anode Current Efficiency	99%

The above run was repeated under the same conditions using a similarly wetted microporous polytetrafluoroethylene manufactured by Doulton Industrial Products Limited. Similar results were obtained.

It will be understood by those skilled in the art that the process of the present invention cannot be used to produce salts where the acid/alkali starting material would attack the separator e.g. hydrogen fluoride would attack the microporous plastics separator. The process also cannot be used to produce insoluble salts unless other means, such as periodic renewal, rotation of the anode or mechanical clearing is carried out since the anode would rapidly become coated with the insoluble product thereby causing the cell voltage to rise and the process to stop. The process furthermore cannot be used where the product is thermodynamically unstable under the cell operating conditions or where the anode is rendered passive by the acid/alkali starting material.

CLAIMS

1. A process for the manufacture of a metal salt, which process comprises passing an electric current through an electrolytic cell comprising an anode formed from or containing the said metal, a cathode, an anolyte which will provide the anions to form the salt and a catholyte, the anode and the cathode being separated by a microporous plastics separator which has a pore size in the range of from 0.01 to 10 microns and a pore volume in the range of from 45 to 55%.

2. A process as claimed in claim 1 wherein the anode is an ingot of the metal whose salt is to be produced.

3. A process as claimed in claim 1 wherein the anode is granulated metal or scrap pieces of the metal whose salt is to be produced.

4. A process as claimed in claim 1 wherein the anode is a non-soluble anode.

5. A process as claimed in claim 1 wherein the anode comprises granulated or particulate samples of mixed metals.

6. A process as claimed in any one of the preceding claims wherein the cathode is formed from the metal whose salt is to be produced.

7. A process as claimed in any one of the preceding claims wherein the anolyte is an acid.

8. A process as claimed in claim 7 wherein the acid is sulphuric acid, hydrochloric acid, nitric acid or acetic acid.

9. A process as claimed in any one of claims 1 to 6 wherein the anolyte is an alkali.

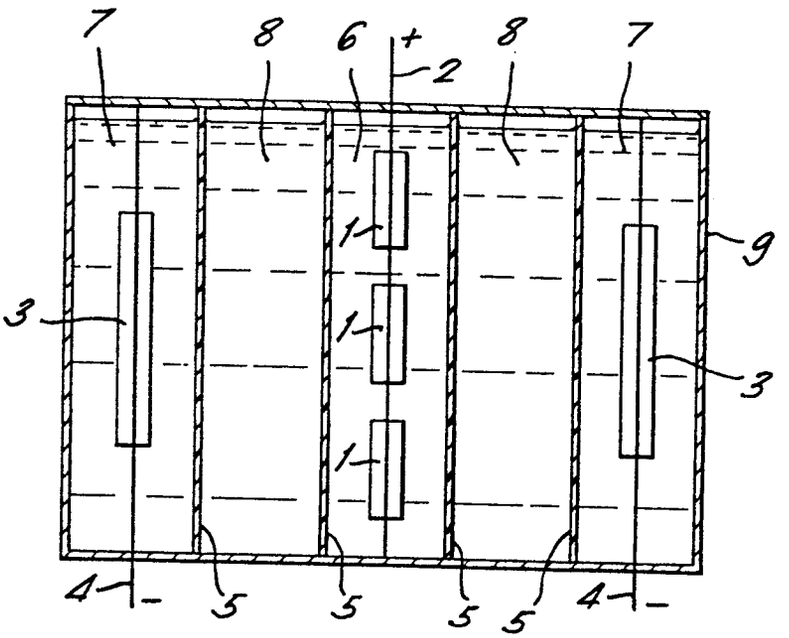
10. A process as claimed in claim 9 wherein the alkali is sodium hydroxide, potassium hydroxide or ammonium hydroxide.

11. A process as claimed in any one of the preceding claims wherein the catholyte is an electrolyte which is the same as the anolyte.

12. A process as claimed in any one of the preceding claims wherein the microporous plastics separator has a pore size in the range of from 0.01 to 0.1 microns and a pore volume of about 50%.

13. A process as claimed in any one of the preceding claims wherein the microporous plastics separator is made from a plastics material which is wettable or which can be treated to render it wettable.

14. A process as claimed in any one of the preceding claims which is carried out continuously or semi-continously.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EUROPEAN SEARCH REPORT

Application number: 0221685

EP 86 30 7734

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	CHEMICAL ABSTRACTS, vol. 99, no. 2, July 1983, page 445, abstract no. 12805y, Columbus, Ohio, US; & RO-A-62 727 (INTREPRINDEREA CHIMICA "DUDESTI") 20-10-1977 * The whole abstract *	1,4,6, 12-14	C 25 B 1/00
Y	GB-A-2 027 637 (ASAHI KASGI KOGYO K.K.) * Page 4, line 62 - page 5, line 20; page 8, lines 15-23 *	1,4,6, 12-14	
A	DE-A-1 902 723 (RUTHNER INDUSTRIEPLANNINGS AG) * Page 2; page 8, examples *	1,2,4-8,11, 14	
A	US-A-1 788 512 (FIREMAN) * Page 2, lines 5-39,74-82 *	1,2,14	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 25 B H 01 M
A	US-A-3 795 595 (WILSON) * Column 2, lines 43-50; column 3, lines 44-59 *	1-3,7, 8,11, 14	
A	US-A-2 288 503 (FRANKLIN) * Page 1, line 31 - page 2, line 5; page 3, lines 13-17; claim 1 *	1,2,9, 10,14	

-/-

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27-01-1987	COOK S.D.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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EUROPEAN SEARCH REPORT

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Application number

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-4 067 788 (SOLOMON)		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27-01-1987	COOK S.D.

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