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(54) Title: PREPARATION OF HYDROLYSED ZIRCONIUM SALT PRECURSORS AND HIGH PURITY ZIRCONIA

(57) Abstract

In the economic production of hydrolysed zirconiferous precipitate, hydrolysis is carried out by the addition of base to aqueous acidic zirconium sulphate solution, to lower the H^+ to and maintain within a pH range of 3 to 7, preferably within 4 to 6. The base may be selected from ammonia, basic ammonium salts, e.g., ammonia-buffered ammonium salts, an alkali metal hydroxide, carbonate or bicarbonate. Specific bases include ammonia and ammonium/sodium/potassium hydroxide, carbonate or bicarbonate, with particular preference for ammonia and ammonium/sodium hydroxide. The starting materials may be incorporated in batchwise or continuous fashion, batchwise by combining them in a body of water, suitable electrolyte or solvent with thorough continuous mixing or continuously by mixing them together in a flowing stream. An additive in the form of an inorganic stabiliser or an organic surfactant may also be included. Inorganic stabilisers may be selected from one or more of Y_2O_3, Ce_2O_3, Al_2O_3, MgO and CaO or precursors thereof. In the finishing stage, either further base may be added to lower residual sulphate content or acid added to remove acid-soluble impurities. The precipitated product is then separated, (e.g., by filtration), washed and calcined to give pure zirconia. High purity zirconia has particular application in the electronics industry and for the production of partially stabilised zirconia ceramics.

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PREPARATION OF HYDROLYSED ZIRCONIUM SALT PRECURSORS AND HIGH PURITY ZIRCONIA

This invention relates to a process for the preparation of zirconium dioxide (zirconia; ZrO_2), and is particularly concerned with the preparation of hydrolysed zirconium-containing materials which are useful intermediates in the preparation of zirconium compounds and processes for the preparation of such products.

There is considerable demand for high purity zirconia for use in the electronics industry and in the production of partially stabilized zirconia. Much of the world's supply of zirconia is obtained from the naturally occurring mineral zirconium silicate (zircon; $ZrSiO_4$) and the processes currently used to extract zirconia from zircon in general involve the thermal decomposition of zircon to give zirconia and silica or the chemical decomposition of zircon to give zirconia and derivatives of silica. However, the crude zirconia produced in this

manner requires purification by further chemical treatment.

Thermal dissociation of zircon to give a mixture of zirconia and silica offers an economically attractive route to zirconia. The dissociated zircon product can be leached with a strong base such as caustic soda in order to dissolve the silica and leave zirconia or can be leached with a strong acid such as sulphuric acid to dissolve the zirconia and form a zirconium salt leaving undissolved silica. The caustic-leach process produces zirconia which may have a purity as high as 99.5% but needs to be subjected to further chemical processing (typically involving dissolving the zirconia in an acid) to produce high purity zirconia. The acid-leaching process has the advantage of producing an acidic solution of a zirconium salt or a water soluble zirconium salt which may be further processed to produce high purity zirconium compounds including zirconia.

It is known in the art to produce zirconia from zirconium sulphate solution by precipitation of the zirconium as a hydrous zirconium oxide (usually retaining some sulphate) by the addition of a base and calcining the precipitated product. However, in practice it has been found that the precipitates formed in this manner are gel-like and difficult to filter.

It is an object of the present invention to provide a method of preparing a precipitated hydrated zirconium-containing material from acidic zirconium sulphate solutions, which may be readily collected by filtration.

A further object is to provide a method which gives

the precipitated product in a form which, by virtue of its particle size and morphology, is particularly suitable for further processing to produce a commercially acceptable zirconia product.

A further object is to provide a method by which other compounds (organic or inorganic) can be intimately mixed with, or co-precipitated with the precipitated product.

We have now found that a precipitated zirconium-containing product having such desirable characteristics can be prepared by treatment of zirconium sulphate solutions with a base using a method of "simultaneous addition" wherein solutions of the sulphate and the base are mixed together in such a way that the combined solution is maintained at substantially constant pH.

The desirable effects obtained by this method are observable over a range of pH value extending from about 3 to 7, with the optimum range being about 4 to 6, depending on the particular reaction conditions.

Accordingly, the present invention provides a process for obtaining a hydrolysed zirconium-containing precipitate from an aqueous zirconium sulphate solution, which comprises combining said solution with a solution of a base in such a manner that the pH of the combined solutions is at all times in the range 3 to 7, preferably 4 to 6, and collecting the precipitate which forms.

Any suitable base may be used including: ammonia; basic ammonium salts, for example, ammonium hydroxide,

ammonium carbonate or ammonium bicarbonate; and the alkali metal hydroxides, carbonates and bicarbonates, for example, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate or potassium bicarbonate.

The preferred method of combining the solutions comprises adding the solutions simultaneously to a suitable vessel, which may initially contain a body of water or any other suitable electrolyte or solvent. Alternatively the solutions may be continuously added and mixed together in a flowing stream, e.g., in a tube or other suitably configured vessel or conduit.

Obviously thorough and continuous mixing of the solutions is essential.

The exact nature of the precipitate and the pH at which optimal precipitation occurs will vary with the reaction conditions. Those conditions include the chemical composition of the zirconium sulphate solution (both the absolute concentrations of zirconium and sulphate and their relative ratio), the nature and concentration of the base used to effect precipitation, temperature, agitation intensity, the geometry of the reactor vessel, ionic strength, addition rates, aging and overall solids concentration in the precipitation suspension.

If desired, additives can be intimately incorporated into the product during precipitation either by dissolution in the zirconium sulphate or base solution prior to precipitation, or by simultaneous addition as a separate stream during precipitation. Such additives may include, for example, inorganic stabilizing compounds e.g.

Y_2O_3, Ce_2O_3, Al_2O_3, MgO, CaO or mixtures of any two or more such oxides, and organic substances, such as, surfactants, which may be desirable or useful in subsequent processing steps or in the final product. Inorganic compounds, such as the oxides referred to above, may be added as such or in the form of precursors thereof which are converted into the required compounds during the precipitation reaction and/or subsequent process steps, such as calcination.

The direct result of the simultaneous addition procedure is an amorphous precipitate which still contains considerable sulphate and has a composition corresponding approximately to the empirical formula $[Zr(OH)_{3+x}]_2(SO_4)_{1-x}$, where x is typically 0 to 0.5.

After precipitation has been completed, further base can be added to lower the residual sulphate content of the precipitate. Alternatively the pH of the suspension can be lowered by addition of acid, with consequent dissolution of acid-soluble impurities. The desirable qualities of the precipitate are not destroyed (and in some cases are enhanced) by this further addition of acid or base, providing the pH has been maintained at the specified level during the initial simultaneous addition.

The precipitated product may be easily separated, e.g., by filtration, from the mixed solutions at any desired stage after the simultaneous addition is complete and may then be calcined directly to give a substantially pure zirconia product (some residual sulphate may still be present). The inherent filterability of the product makes it amenable to subsequent washing and, hence, reduction of

impurity levels.

The nature of the zirconium sulphate solution is not critical. Solutions obtained by any known sulphate leaching procedure may be used, including the solutions obtained by the procedures described in International Patent Application No. PCT/AU86/00018. Sulphate solutions obtained by dissolving zirconium compounds in water or sulphuric acid solutions may also be used, including the solutions obtained by dissolving compounds described in International Patent Application No. PCT/AU86/00109.

The invention is further described and illustrated in the following non-limiting examples.

Example 1

An acidic zirconium sulphate solution containing 100g/l ZrO_2, 120g/l SO_4 and 14g/l NH_3 at a pH of approx. 1.5, was prepared by dissolving $(NH_4)_2(ZrO)_2(SO_4)_3$ (see International Patent Application No. PCT/AU86/00109). This solution and a 4% w/w ammonia solution were simultaneously added to a stirred $200cm^3$ reservoir of water at such relative rates that the pH of the resulting suspension remained essentially constant at 5.2.

In a standard filtration test, 300g of the above suspension containing 20g ZrO_2 filtered in 36 seconds through a 7cm Buchner funnel with two layers of Whatman GF/A glass filter paper.

The dried precipitate contained 20% w/w sulphate.

Example 2

This example shows the effect of varying the pH at which precipitation is carried out.

The procedure described in Example 1 was repeated at various constant pH values. The filtering times recorded using the standard filtering test of Example 1 are tabulated below.

pH	3.5	3.8	4.7	5.2	5.8	6.8	7.5
Filtering time (sec)	>300	225	48	36	41	240	>300

Example 3

This example (which should be compared with Examples 1 and 2) shows the effect of varying solution compositions on the optimum precipitation pH.

An acidic zirconium sulphate solution (200g/l ZrO_2, 500g/l SO_4, pH approx. 0) and a 31% w/w ammonia solution were simultaneously added to a stirred 500cm^3 reservoir of water at such relative rates that the pH of the resulting suspension remained essentially constant at the pre-selected value. The standard filtration test used was similar to that in Example 1 except that a 15cm funnel and filter papers were used. Filtering times were measured using 1.8l of a suspension containing 35g/l ZrO_2. The filtering times at different pH values are tabulated below.

pH	3	3.5	4	4.5	5	7	8	9
Filtering time (min)	>60	10	4	3.5	4	20	25	25

Example 4 (Comparative Example)

This example shows the effect of adding a zirconium sulphate solution to a pre-existing ammonia solution; compare with Example 3 showing simultaneous addition, in accordance with the invention.

An acidic zirconium sulphate solution (200g/l ZrO_2, 500g/l SO_4, pH approx. 0) was added to a stirred reservoir containing 500cm^3 of water and 125cm^3 of 31% w/w ammonia solution until the suspension pH reached a value of 5. In the standard filtration test described in Example 3, this suspension took 3 hours to filter.

Example 5 (Comparative Example)

This example shows the effect of adding ammonia to a pre-existing zirconium sulphate solution; compare with Example 3 showing simultaneous addition, in accordance with the invention.

A 31% w/w ammonia solution was added to a stirred reservoir containing 500cm^3 of water and 320g of an acidic zirconium sulphate solution (200g/l ZrO_2, 500g/l SO_4, pH approx. 0) until the suspension pH reached a value of 5. In the standard filtration test described in Example 3, this suspension took 45 minutes to filter.

Example 6

This example shows the effect of raising the pH, after initial precipitation, on product sulphate levels and filtering time.

The procedure described in Example 1 was used to prepare a suspension at pH 5.2. The pH of the suspension was then raised to a value of 9.2 by further addition of ammonia. In the standard filtration test described in Example 1, the above suspension filtered in 25 seconds.

The dried precipitate contained 4.8% w/w sulphate.

Example 7

This example shows the effect of lowering the pH, after initial precipitation, on filtering time and impurity levels in the product.

The procedure described in Example 3 was used to prepare a suspension at pH 4.5. The pH of the suspension was then lowered to a value of 2.5 by addition of H_2SO_4. In the standard filtration test described in Example 3 this suspension took 10.5 minutes to filter.

Impurities present in pH 4.5 precipitate (ppm)

Y	U	Fe	Ti	Al
1340	350	240	260	440

Impurities present in precipitate after pH lowered to 2.5 (ppm)

Y	U	Fe	Ti	Al
380	130	230	260	250

Example 8

This example shows the use of sodium hydroxide in place of ammonia.

An acidic zirconium sulphate solution (200g/l ZrO_2, 500g/l SO_4, pH approx. 0) and a 34% w/w NaOH solution were simultaneously added to a stirred 500cm^3 reservoir of water at such relative rates that the pH of the resulting suspension remained essentially constant at pH 5. In the standard filtration test described in Example 3, this suspension took 4 minutes to filter.

Example 9

This example shows the co-precipitation of magnesia with zirconia.

An acidic zirconium/magnesium sulphate solution containing 100g/l ZrO_2, 3.6 g/l MgO, 120g/l SO_4 14 g/l NH_3, and having a pH of approx. 1.5, was reacted with a 4% w/w NH_3 solution at pH 5.2 as described in Example 1. The pH of the suspension was then raised to a value of 9.2 by further addition of ammonia. In the standard filtration test described in Example 1, the above suspension filtered in 26 seconds.

After calcination at 1000°C for 2 hours the magnesia doped product contained 3.4% w/w MgO.

Example 10

This example shows the co-precipitation of yttria with zirconia.

An acidic zirconium/yttrium sulphate solution containing 100g/l ZrO_2, 5.5g/l Y_2O_3, 120g/l SO_4, 14g/l NH_3, and having a pH of approx. 1.5, was reacted with a 4% w/w NH_3 solution as described in Example 1. In the standard filtration test described in Example 1, the above suspension filtered in 32 seconds.

After calcination at 1000°C for 2 hours, the yttria-doped product contained 3 mole % Y_2O_3 and existed substantially in the tetragonal crystalline state.

The product prepared in Example 1, when calcined at 1000°C for 2 hours, existed substantially in the monoclinic crystalline state.

Example 11

This example shows a pilot plant experiment where in comparison with the preceding Examples,

(i) the overall reaction time was longer,
(ii) the agitation was less intense, and
(iii) the geometry of the reactor vessel was different.

All of these factors combined to give a product of greater filterability.

An acidic zirconium sulphate solution (as described in Example 1) and a 4% w/w ammonia solution were simultaneously added to a gently stirred 250 litre reservoir of water at such relative rates that the pH of the resulting suspension remained essentially constant at 5.2 until an equivalent of 35kg ZrO_2 had been precipitated over a period of 90 minutes. In the standard filtration test described in Example 1, the above suspension filtered in 16.5 seconds.

Example 12

This example shows how the process of the invention can be performed as a continuous process.

An acidic zirconium sulphate solution (as described in Example 1) and a 4% w/w NH_3 solution were simultaneously added to a stirred overflow vessel at such relative rates that the pH of the resulting suspension remained essentially constant at 5.2.

The rates of addition of reactant solutions and the volume of the overflow vessel were such that they gave an average residence time of approximately 5 min. In the standard filtration test described in Example 1, the above suspension filtered in 25 sec.

CLAIMS

1. A process for obtaining a hydrolysed zirconium-containing precipitate from an aqueous zirconium sulphate solution, characterised in that the solution is combined with a solution of a base in such a manner that the pH of the combined solutions is maintained at all times in the range 3 to 7, and collecting the precipitate which forms.

2. A process as claimed in Claim 1, characterised in that the pH of the combined solutions is maintained in the range 4 to 6.

3. A process as claimed in Claim 1 or Claim 2, characterised in that the base is ammonia, a basic ammonium salt, or an alkali metal hydroxide, carbonate or bicarbonate.

4. A process as claimed in any one of Claims 1 to 3, characterized in that the base is selected from ammonia, ammonium hydroxide, ammonium carbonate, ammonium bicarbonate, sodium hydroxide, sodium carbonate, sodium bicarbonate, potassium hydroxide, potassium carbonate and potassium bicarbonate.

5. A process as claimed in any one of Claims 1 to 4, characterized in that the base is selected from ammonia, ammonium hydroxide and sodium hydroxide.

6. A process as claimed in any one of Claims 1 to 5, characterised in that the solutions are combined by adding

the solutions simultaneously, with thorough and continuous mixing, to a suitable vessel, which optionally contains initially a body of water or any other suitable electrolyte or solvent.

7. A process as claimed in any one of Claims 1 to 6, characterised in that the solutions are combined by continuously mixing them together in a flowing stream.

8. A process as claimed in any one of the preceding Claims, characterised in that an additive is incorporated into the product during precipitation, either by dissolution in the zirconium sulphate or base solution prior to precipitation, or by simultaneous addition as a separate stream during precipitation.

9. A process as claimed in Claim 8, characterised in that the additive is an inorganic stabilizing compound.

10. A process as claimed in Claim 9, characterised in that the additive is Y_2O_3, Ce_2O_3, Al_2O_3, MgO, CaO or a mixture of two or more such oxides or precursors thereof.

11. A process as claimed in Claim 8, characterised in that the additive is an organic surfactant.

12. A process as claimed in any one of the preceding Claims, characterised in that after precipitation has been completed, further base is added to lower the residual sulphate content of the precipitate.

13. A process as claimed in any one of Claims 1 to 11, characterised in that after precipitation has been

completed, the pH of the suspension is lowered by addition of acid, with consequent dissolution of acid-soluble impurities.

14. A hydrolysed zirconium-containing precipitate produced by combining an aqueous zirconium sulphate solution with a solution of a base in such a manner that the pH of the combined solutions is maintained at all times in the range 3 to 7, and collecting the precipitate which forms.

15. Zirconia produced by calcining the product of Claim 14.

INTERNATIONAL SEARCH REPORT

International Application No PCT/AU 87/00163

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] C01G 25/06 / C01G 25/02

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	C01G 25/06, C01G 25/02, C01G 25/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [8]

AU : IPC as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	AU,B1, 117741 (6512/42) (F.W. BERK & CO. LTD) 25 November 1943 (25.11.43) see page 2 lines 15-24 and page 4 lines 14-19	(1-6,14,15)
P,A	AU,A1, 53972/86 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION)14 August 1986 (14.08.86) see Claims 7 and 14-16 and page 7 lines 10-17 and 26-30	(1-6,12,14,15)
P,A	AU,A1, 58667/86 (ICI AUSTRALIA LTD) 6 November 1986 (06.11.86) see the claims	(1-7,14,15)
P,A	DD,A1, 239396 (AKADEMIE DER WISSENSCHAFTEN DER DDR) 24 September 1986 (24.09.86) see the examples	(1-4,8-10,14,15)
A	EP,A1, 79458 (DYNAMIT NOBEL AKTIENGESELLSCHAFT) 25 May 1983 (25.05.83) see Claims 1-3, page 6 and page 7 lines 1-9	(1-5,12,14,15)
A	EP,A2, 171736 (NIPPON SHOKUBAI KAGAKU KOGYO CO. LTD) 19 February 1986 (19.02.86) see the claims and the examples	(1-6,8-10,14,15)
X	GB,A, 1495267 (BORAX CONSOLIDATED LIMITED) 14 December 1977 (14.12.77) see the full specification	(1-4,6,12,14)

(continued)

* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
14 September 1987 (14.09.87)	(25.09.87) 28 SEPTEMBER 1987
International Searching Authority	**Signature of Authorized Officer**
Australian Patent Office	R.A. MELVIN

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document with indication where appropriate, of the relevant passages	Relevant to Claim No
A	METADEX Database, DIALOG SEARCH SERVICE, (Metals Abstracts, American Society for Metals & The Metals Society, London), Accession No. 85-421331, N.V. Baryshaikov et al, 'Production of Zirconium Hydroxide from Basic Sulphate', Abstract No. 948287, Tsvetn. Mef. 1985 (3) 64-65 (Russ.)	(1-6,12,14)
X	Patent Abstracts of Japan, C-197, page 163, JP,A2, 58-151327 (SHIN NIPPON RIKA K.K.) 8 September 1983 (08.09.83)	(1,2,8,9,14)
X	Patent Abstracts of Japan, C-289, page 136, JP,A2, 60-36330 (ONODA CEMENT K.K.) 25 February 1985 (25.02.85)	(1-5,12,14,15)
A	US,A, 3961026 (V.N. POKHODENKO, N. TSELIK) 1 June 1976 (01.06.76) see the claims	(1-4,14)
X	US,A, 4283377 (J. FENNER) 11 August 1981 (11.08.81) see the claims and the examples	(1-4,13-15)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 87/00163

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report	Patent Family Members		
AU 53972/86	WO 8604614	EP 210236	
AU 58667/86	WO 8606362 A 8602781	CN 86103022	ZA 861126
EP 79458	DE 3143921	DK 4761/82	JP 58084120
EP 171736	JP 61044718	US 4664894	JP 61286222
GB 1495267	CA 1042179 JP 50127897	DE 2510743 ZA 7501656	FR 2264780
US 4283377	FR 2460894	GB 2051767	ZA 8003450

END OF ANNEX