

TRANSLATION OF GRANTED EUROPEAN PATENT No 0 334 732
(application No 89400755.8 filed on March 17, 1989)

Novel reactive derivate of zirconium and its preparation

5 The invention relates to a new reactive derivative of zirconium and to its preparation.

The term "reactive derivative of zirconium" denotes a zirconium compound which is in solution in an aqueous or organic solvent or can be dissolved in such a solvent. The reactive derivative of zirconium can
10 react in the dissolved state with other compounds.

Many reactive derivatives of zirconium are known. Among these, those most commonly employed in industry are the following:

basic zirconium carbonate ($\text{CO}_2/\text{ZrO}_2 \simeq 0.5$) containing 40% by weight of ZrO_2 , in the form of moist
15 paste,

zirconium orthosulphate ($\text{sulphate}/\text{ZrO}_2 \simeq 2$) either in the form of aqueous solution (containing 18% by weight of ZrO_2), or in the form of crystallized
20 solid (containing 32% by weight of ZrO_2),

zirconium oxychloride ($\text{chloride}/\text{ZrO}_2 \simeq 2$) either in the form of aqueous solution (containing 20% by weight of ZrO_2) or in the form of crystallized solid (containing 33% by weight of ZrO_2),

25 basic zirconium sulphate ($\text{sulphate}/\text{ZrO}_2 \simeq 0.6$ to 1) in the form of moist paste (containing 37% by weight of ZrO_2),

zirconium nitrate in the form of aqueous solution (containing 19% by weight of ZrO_2) or of solid
30 (containing 40% by weight of ZrO_2),

zirconium acetate in solution (containing 22% by weight of ZrO_2),

zirconium hydroxide (containing 42% by weight of ZrO_2), and

zirconium ammonium carbonate in solution (containing 13% by weight of ZrO_2).

Many organic derivatives of zirconium are also known (propionate, lactate, acetylacetonate, various 5 alcoholates), whose ZrO_2 content ranges from 6 to 15% by weight.

These materials are employed as such (in the case of derivatives in solution) or must be dissolved by reaction with a solution, generally acidic, by the 10 final user (in the case of derivatives which are solid or in paste form).

In practice, only the zirconium present in the abovementioned materials is generally utilized, and not the anions (for example chloride, carbonate, sulphate, 15 nitrate or acetate) and/or the water, even though they form the greater part of these materials, their role being essentially to keep the zirconium in a soluble form. The anions and/or the water do not directly participate in the reactions involved in the practical 20 applications of these materials and are, in fact, rather detrimental. In fact, solutions of zirconium compounds are corrosive and toxic, and this presents problems in storage and in transport, and pastes based on zirconium compounds are heterogeneous because of the 25 presence of free water and are difficult to handle. Furthermore, certain anions (particularly sulphates and chlorides) or water can oppose the required reactions, for example during the production of driers of the zirconium soap type. Finally, from an economic standpoint, 30 it is not very advantageous to transport materials containing relatively little active material (ZrO_2) and to have to employ costly containers capable of resisting corrosion, in the case of materials in the form of solutions or of pastes.

35 It is therefore advantageous to be able to have available reactive derivatives of zirconium with a high ZrO_2 content, which are solid materials containing a minimum of impurities and of water.

The objective of the invention is to provide such reactive derivatives of zirconium.

More particularly, the invention relates to reactive derivatives of zirconium, characterized in that they are in the form of a pulverulent white solid which is not crystallized and dry in appearance, soluble in an aqueous solution of an acid, and consist of metazirconic acid $\text{ZrO}(\text{OH})_2$ accompanied by free or weakly bound water, wherein some of the OH^- ions have been replaced by halide ions, the ZrO_2 content of these derivatives being from 60 to 92% by weight inclusive, preferably from 75 to 86.5% by weight, and the water content of these derivatives ranging from 3 to 39.98%, preferably 13 to 25%, and the halide ion content of these derivatives ranging from 0.02% to approximately 5% by weight.

A class of preferred derivatives is that of the derivatives containing, on a weight basis, 75 to 86.5% of ZrO_2 , 13 to 25% of water and not more than approximately 0.5% of halide ions, in particular Cl^- ions. Another class of preferred derivatives is that of the derivatives containing, on a weight basis, less than 13% of water and more than 0.5% of halide ions, in particular Cl^- ions.

The invention also relates to a process for the preparation of the abovementioned reactive derivatives of zirconium, characterized in that it comprises the steps consisting of:

a) preparing water-rich zirconia hydrate $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$ or zirconium hydroxide $\text{Zr}(\text{OH})_4$,

b) replacing some of the OH^- ions of the product of step (a) with halide ions, and

c) partially dehydrating, in a controlled manner, the product of step (b) by heating to a temperature of not more than 130°C until a pulverulent white solid is obtained, which is not crystallized and dry in appearance and soluble in an aqueous solution of an acid.

The first step (a) consists in preparing

water-rich zirconia hydrate $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$, also called zirconium hydroxide $\text{Zr}(\text{OH})_4$. "Water-rich" means a product containing at least 45% by weight of water in total (free water + bound water). This step may be performed in various ways, such as, for example:

- Neutralization of an acidic aqueous solution of a Zr salt (for example the oxychloride, nitrate or acetate), with a base (for example sodium hydroxide, aqueous ammonia), followed by filtration and washing of the filter cake. A bulky and water-rich (90% and more) precipitate of zirconia hydrate or zirconium hydroxide is thus obtained.

This method offers the advantage of providing a pure product freed from the impurities which may be present in the starting salt.

- Hydrolysis of an organic zirconium salt in solution in water or a water-alcohol mixture, followed by filtration and washing of the filter cake. However, this method is not the most advantageous from an economic standpoint, because an organic Zr salt must be available.

- Displacement of ions from a solid basic Zr salt with a reactant in aqueous solution or water, depending on circumstances, followed by filtration and washings of the filter cake. A "basic" Zr sulphate (reactant: base in aqueous solution) or an alkali metal zirconate such as sodium zirconate (reactant: water) may be employed, for example, as a basic Zr salt. This method is the preferred method from the point of view of cost. It also makes it possible to obtain a reactive derivative of zirconium with a reduced content of free or weakly bound water. It has the possible disadvantage of leaving fairly high residual contents of sulphates in the product, (in the case of a basic Zr sulphate) or of alkali metal oxides (in the case of an alkali metal zirconate). However, when the step (b) is carried out, the alkali metal oxides are found to be practically eliminated.

The step (b) of partial substitution of the OH^- ions in the product of step (a) by halide ions makes it possible to obtain reactive derivatives of zirconium with higher ZrO_2 contents.

5 This step can be conducted by washing the product of step (a) with an aqueous solution of the corresponding hydrohalogenic acid. In the case of washing with hydrochloric acid which is intended to substitute Cl^- ions for OH^- ions, a Cl^- ion content of the order of 5% by
10 weight can be attained, but the final content can be adjusted by carrying out a second washing with the aid of aqueous ammonia, for example. In the case where the product of step (a) has been obtained by displacement of ions from an alkali metal zirconate, such as Na
15 zirconate, the substitution of OH^- ions by halide ions, for example Cl^- , can be carried out by washing the product of step (a) with an aqueous solution of ammonium halide, for example ammonium chloride, optionally acidified with hydrochloric acid. The
20 residual sodium is thus displaced with a controllable quantity of Cl by adjusting the pH of the washing solution. A subsequent washing with another acid allows the corresponding anions to be fixed, even if the latter do not contribute to the stability (in the case
25 of washing with HNO_3 in example 5).

The controlled dehydration step (c) may also be performed in various ways. This dehydration may be carried out merely by heating the product of step (b) in an oven at a temperature not exceeding 130°C in the case of a
30 relative atmospheric humidity of 50 to 70%. The dehydration begins already at 30°C but is slow at this temperature. The operation will be preferably carried out between 80 and 110°C . The degree of dehydration obtained will obviously vary with the temperature employed and the
35 degree of heating. The dehydration can also be performed by heating using microwaves. This heating method

is highly effective and rapid. An excessively severe heating, which would result in the decomposition of $\text{ZrO}(\text{OH})_2$ with production of insoluble zirconia (that is to say of crystallized zirconia) and water, must be avoided in any case.

The reactive derivatives of zirconium of the invention can be easily converted into the usual reactive derivatives of zirconium. It suffices to dissolve the derivatives of the invention in an aqueous solution of an acid, for example of hydrochloric acid to obtain zirconium oxychloride, of nitric acid to obtain zirconium nitrate, and so on. The high solubility of the derivatives of the invention can be attributed to the presence of zirconyl ions ZrO^{2+} .

The reactive derivatives of zirconium of the invention are remarkably stable. After a period of 15 days at 80°C , their solubility in a hydrochloric acid solution remains higher than 95%, whereas it is then only 50% in the case of basic zirconium carbonate.

Depending on their purity, the derivatives of the invention can be employed as a source of Zr in various industrial applications. By way of indication, there may be mentioned:

- the treatment of TiO_2 -based pigments, the derivative of the invention being dissolved in situ in a hydrochloric or sulphuric medium,
- the treatment of petroleum formations, it being possible for the derivative of the invention to be dissolved on site in hydrochloric acid.

The following examples, which do not imply any limitation, are given for illustrating the invention..

Example 1

55 parts by weight of zirconia (natural oxide known as baddeleyite or thermal oxide) with an average particle size of 0.6 to $15\ \mu\text{m}$ are mixed with 45 parts by weight of NaOH in the form of solid pellets or of concentrated aqueous solution. The mixture is heated to 850°C for 1 hour to obtain, after cooling, a solid mix-

ture of sodium zirconate and excess sodium hydroxide. This mixture is brought into contact with water at 60°C, with stirring (water/mixture weight ratio: 2.5/1). The suspension obtained is filtered and the filtration residue is then washed in a stream of water (water/product weight ratio: 20/1). The product obtained is washed with a 0.1N aqueous solution of HCl (solution/product weight ratio: 30/1), and then with water (water/product weight ratio: 5/1). The moist paste obtained is then dehydrated for 24 hours at 40°C at 50-70% relative humidity. The pulverulent solid product finally obtained contains, on a weight basis, approximately 75% of ZrO_2 , 20% of H_2O , 5% of Cl^- and less than 0.5% of various impurities.

Example 2

The operating procedure of example 1 is repeated as far as the first washing of the filtration residue with water, inclusive. The product obtained is then washed with a concentrated (100 g/l) solution of ammonium chloride (NH_4Cl solution/product weight ratio: 3/1) and then with water (water/product weight ratio: 5/1). The resulting product is then dehydrated by heating to 80°C for 6 hours at 50-70% relative humidity. The pulverulent solid product finally obtained contains, on a weight basis, 84% of ZrO_2 , 15% of H_2O , 0.5% of Cl^- and approximately 0.5% of impurities (mainly Na_2O).

Example 3

The operating procedure of example 1 is repeated as far as the first washing of the filtration residue with water, inclusive. The product is then dehydrated at 80°C for 12 hours at 50-70% relative humidity. The pulverulent solid product finally obtained contains, on a weight basis, 82% of ZrO_2 , 13% of H_2O and 5% of Cl^- and less than 0.5% of impurities (mainly Na_2O).

Example 4

1 kg of basic zirconium sulphate, obtained as described by F. Farnworth, S.L. Jones, I. McAlpine, "The production, properties and use of zirconium chemicals", Special Publication of the Royal Soc. of Chemistry, No. 40, p. 259 (1981), is suspended in 9 litres of 0.1N aqueous ammonia solution. The pH of the mixture obtained is approximately 7. After stirring at 25°C the product is filtered and the filter cake is washed with 5 litres of water. The product obtained is then dried at 80°C for 12 hours at 50-70% relative humidity. The solid product finally obtained contains, on a weight basis, 82% of ZrO_2 , 13% of H_2O and 5% of impurities (mainly sulphate ions). It should be noted that the aqueous ammonia could be replaced with another base.

Example 5

The operating procedure of example 1 is repeated as far as the first washing of the filtration residue with water, inclusive. The product obtained is washed with a 0.1N aqueous solution of nitric acid (acid solution/product weight ratio: 30/1). The product is then dehydrated at 80°C for 12 hours at 50-70% relative humidity. The pulverulent solid product finally obtained contains, on a weight basis, 82% of ZrO_2 , 13% of H_2O and 5% of impurities (mainly nitrate ions).

Example 6

The operating procedure of example 1 is repeated as far as the washing with hydrochloric acid, inclusive. The product is then dehydrated at 120°C for 12 hours at 50-70% relative humidity. The pulverulent solid product finally obtained contains, on a weight basis, approximately 92% of ZrO_2 , 3% of H_2O , 5% of Cl^- and less than 0.5% of impurities.

Example 7 Preparation of a zirconium oxychloride solution containing 20% of ZrO_2

The product of example 2 is added to a 37% strength aqueous solution of hydrochloric acid in such quantities that the molar ratio Cl/ZrO_2 is equal to

approximately 2; the whole is heated to 100°C for 30 minutes and water is then added to adjust the relative density of the resulting solution to 1.37, and the latter is then cooled to ambient temperature.

5 Example 8 Preparation of a zirconium nitrate solution containing 20% of ZrO_2

10 The product of example 2 is added to a 65% strength aqueous solution of nitric acid in such quantities that the molar ratio NO_3/ZrO_2 is equal to approximately 2 and that the proportion of ZrO_2 is approximately 20% by weight. The whole is heated to 80°C for 1 hour and is then cooled to ambient temperature.



CLAIMS

1. Reactive derivatives of zirconium, characterized in that they are in the form of a pulverulent white solid which is not crystallized and dry in appearance, soluble in an aqueous solution of an acid, and consist of
5 metazirconic acid $\text{ZrO}(\text{OH})_2$, accompanied by free or weakly bound water, wherein some of the OH^- ions have been replaced by halide ions, the ZrO_2 content of these derivatives being from 60 to 92 % by weight inclusive, the water content of these derivatives ranging from 3 to 39.98
10 %, and the halide ion content of these derivatives ranging from 0.02 % to approximately 5 % by weight.
2. Reactive derivatives of zirconium according to claim 1, characterized in that they contain, on a weight basis, 75 to 86.5 % of ZrO_2 , 13 to 25 % of water and not more
15 than approximately 0.5 % of halide ions.
3. Reactive derivatives of zirconium according to claims 1, characterized in that they contain more than 0.5 % by weight of halide ions and a proportion of water which is lower than 13 % by weight.
- 20 4. Derivatives according to claim 1, characterized in that the halide ions are Cl^- ions.
5. Process for the preparation of a reactive derivative of zirconium, characterized in that it comprises the steps consisting of :
25 a) preparing water-rich zirconia hydrate $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$ or zirconium hydroxyde $\text{Zr}(\text{OH})_4$,
 b) replacing some of the OH^- ions of the product of step (a) with halide ions, and



c) partially dehydrating, in a controlled manner, the product of step (b) by heating to a temperature of not more than 130°C until a pulverulent white solid is
5 obtained, which is not crystallized and dry in appearance and soluble in an aqueous solution of an acid.

6. Process according to claim 5, characterized in that step (a) is performed by displacement of ions from a solid basic Zr salt with a reactant in aqueous solution or
10 water, depending on circumstances, followed by a filtration and washings of the filter cake.

7. Process according to claim 6, characterized in that the basic Zr salt is a basic Zr sulfate and the reactant in aqueous solution is an aqueous solution of a base.

15 8. Process according to claim 6, characterized in that the basic Zr salt is an alkaline metal zirconate and the reactant is water.

9. Process according to Claim 5, characterized in that step (a) is performed by neutralizing an acidic aqueous
20 solution of a zirconium salt with a base, followed by filtration and washing of the filter cake.

10. Process according to claim 5, characterized in that step (b) is performed by washing the product of step (a) with an aqueous solution of a hydrohalogenic acid or an
25 ammonium halide.

11. Process according to claim 10, characterized in that step (b) is carried out by washing the product of step (a) with an aqueous solution of hydrochloric acid or of ammonium chloride.

30 12. Process according to claim 5, characterized in that the heating is carried out with the aid of microwaves.