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DECISION
of 12 December 1997

Case Number: T 0338/94 - 3.3.5

Application Number: 87119391.8

Publication Number: 0322480

IPC: C01G 43/025

Language of the proceedings: EN

Title of invention:
Method of controlling the crystal grain size of uranium dioxide pellet

Applicant:
Mitsubishi Materials Corporation

Opponent:
-

Headword:
UO_2 pellets/MITSUBISHI MATERIALS CORPORATION

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step (main request, no; auxiliary request, yes)"

Decisions cited:
-

Catchword:
-

Case Number: T 0338/94 - 3.3.5

DECISION
of the Technical Board of Appeal 3.3.5 of 12 December 1997

Appellant:

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Representative:

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Decision under appeal:

Decision of the Examining Division of the European Patent Office posted 29 November 1993 refusing European patent application No. 87 119 391.8 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: R. K. Spangenberg
Members: M. M. Eberhard
J. H. van Moer

Summary of Facts and Submissions

I. European patent application No. 87 119 391.8 was refused by a decision of the Examining Division. The decision was based on amended claims 1 and 2 filed on 16 December 1992 with dependent claims 3 and 4 submitted on 23 October 1991.

II. The ground for the refusal was that the subject-matter of claim 1 did not meet the requirement of inventive step having regard to the teaching of D1 (Chemical Abstracts, vol. 109, 1988, No. 6, No. 45001m, Abstract of JP-A-62-297 215) and D2 (Chemical Abstracts, vol. 103, No. 6, 1985, No. 44372x).

The Examining Division held that the problem of providing pellets of UO_2 in which the crystal grain size was adjusted to values within the range of from 5 to 100 µm was already solved in D1. The use of uranium concentrations of from 50 to 1000 g/l and the absence of HF to achieve the desired grain size were disclosed in D1. Claim 1 encompassed any adjustment of the pellets' grain size within the broad range of D1, by adding unspecified amounts of uranyl nitrate into the uranyl fluoride solution. In view of the teaching of D2 about the influence of the uranyl fluoride/uranyl nitrate ratio on the particle size distribution of the ammonium diuranate (ADU) precipitate, it was obvious to the skilled person to replace, in the process of D1, an unspecified amount of the uranyl fluoride by uranyl nitrate, while still achieving the desired grain size of 5 to 100 µm. As the desired grain size values were achieved in D1, it had to be assumed that rates of contact with ammonia falling within the claimed range were inherently used.

III. The Appellant lodged an appeal against this decision and filed a statement of grounds of appeal in due time. Two sets of amended claims were filed on 11 November 1997, as main request and first auxiliary request, in reply to a communication from the Board. The Appellant submitted an English translation of JP 62-297 215 (hereinafter D1a) referred to in D1, as well as a copy of the article "Advances in Crystallisation From Solutions", AIChE, Symposium Series 1984, vol. 80, 240, pages 123 to 126 (hereinafter D2a) from which the abstract D2 was derived. Claim 1 of the said main request reads as follows:

"1. A method of controlling the crystal grain size of UO_2 pellets comprising the steps of:

(1) reacting an aqueous uranyl solution with ammonia so as to precipitate ammonium diuranate (ADU), the aqueous uranyl solution comprising uranyl fluoride (UO_2F_2) and being free from hydrofluoric acid and nitric acid,

(2) calcining and reducing said ADU precipitate to form uranium dioxide (UO_2) powder, and

(3) molding and sintering said uranium dioxide powder; characterised in that:

said aqueous uranyl solution further comprises uranyl nitrate $UO_2(NO_3)_2$ and the ratio of uranyl fluoride to uranyl nitrate in said aqueous uranyl solution is adjusted so as to be greater than 0% and less than 100%; the concentration of uranium in the reaction mixture is adjusted between 50 and 1000 gU/liter; and the rate of contact between ammonia and the uranium

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components in said aqueous uranyl solution is adjusted to at least 2 moles NH_3/min/mole U; so that uranium dioxide pellets are produced having a predetermined crystal grain size of 5-100 micrometers."

IV. Oral proceedings were held on 12 December 1997. At the hearing the Board expressed doubts as to whether the process according to claim 1 of the main request met the requirement of inventive step, taking into account that the rate of addition of ammonia and the adjustment of the uranium concentration were known from D1a, and claim 1 encompassed the case where almost no uranyl nitrate was present in the solution. The Appellant abandoned the first auxiliary request filed on 11 November 1997 and submitted, instead, a set of amended claims 1 to 3 as first and sole auxiliary request. Claim 1 thereof reads as follows:

"1. A method of controlling the sintered density and crystal grain size of UO_2 pellets comprising

(1) providing an aqueous uranyl solution which is free of hydrofluoric acid and nitric acid and which contains both uranyl fluoride (UO_2F_2) and uranyl nitrate ($UO_2(NO_3)_2$) as uranium components,

(2) reacting with ammonia said aqueous uranyl solution to precipitate ammonium diuranate (ADU), while adjusting the ratio of said uranium components to a predetermined value, adjusting the concentration of uranium in the reaction mixture to a predetermined value within the range 50 to 1000 gU/liter and also adjusting the rate of contact between said uranium components in said aqueous uranyl solution with ammonia to a predetermined value of at least 2 moles NH_3/min/mole U, the crystal grain size of the pellets being adjusted to the desired value upwards by decreasing the

relative amount of uranyl nitrate in the uranyl solution and/or increasing the rate of contact between the uranium components and ammonia or downwards by increasing the relative amount of uranyl nitrate in the uranyl solution and/or decreasing the rate of contact between the uranium components and ammonia,

(3) calcining and reducing said ADU precipitate to form UO_2 powder, and

(4) molding and sintering said UO_2 powder,
thus producing UO_2 pellets having a predetermined crystal grain size in the range varying from more than 20 to 100 micrometers and a sintered density of 99% of the theoretical density."

V. The Appellant's arguments can be summarised as follows:

The data reported in Table 1 of D1a showed that, in the absence of HF in the uranyl fluoride solution, the sintered density of the UO_2 pellets decreased when the uranium concentration was increased from 500 to 1100 gU/l to produce pellets with a smaller crystal grain size. Therefore, starting from D1a, the problem to be solved was how to control simultaneously the sintered density and the crystal grain size of UO_2 pellets. The solution defined in claim 1 of the main request comprised adjusting the uranyl fluoride to uranyl nitrate ratio and adjusting the rate of contact of ammonia with these components. It was clear from the wording of claim 1 that the process included continuously adjusting the rate of addition of ammonia in order to control the crystal grain size of the UO_2 pellets.

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With the claimed method it was possible to control the crystal grain size of the pellets and the sintered density in a large range even if one of the three parameters, uranyl nitrate/uranyl fluoride ratio, speed of addition of ammonia and concentration of uranium, was fixed. Furthermore, the invention made it possible to control the crystal grain size over a wide range, whilst still obtaining a sintered density of more than 99%. D2a disclosed a method for controlling the particle size distribution of the ADU precipitate by adjusting the uranyl nitrate/uranyl fluoride ratio, but did not suggest the possibility of controlling the crystal grain size and the sintered density of the UO_2 pellets produced therefrom.

According to D1a, an ADU precipitate of small particle size led to sintered UO_2 pellets of large crystal grain size. As, on the other hand, D2a stated that the ADU particles became small when the $UO_2(NO_3)_2/UO_2F_2$ ratio was high, a skilled person might have expected the crystal size of the UO_2 pellets to become larger by increasing the $UO_2(NO_3)_2/UO_2F_2$ ratio. However, in the present invention, the effect resulting from an increase of the said ratio was contrary to this expectation, since the crystal grain size of the pellets became smaller as the $UO_2(NO_3)_2/UO_2F_2$ ratio increased. Therefore, the chemical mechanism of formation of the fine ADU precipitate in a uranyl solution not containing HF according to the present invention was completely different from that described in D2a in the presence of HF. As D2a did not describe the effect of uranyl nitrate on the particle size of ADU precipitates in the absence of HF, a skilled person was unable to combine D2a with D1a with a view to enlarging the particle size of an ADU precipitate, thereby decreasing the crystal grain size of UO_2 pellets. Furthermore, D2a did not suggest the idea of adjusting the speed at which ammonia was added.

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VI. The Appellant requested that the decision under appeal be set aside and that the case be remitted to the first instance with the order to grant a patent on the basis of claims 1 to 4 according to the main request filed on 11 November 1997 (main request), or alternatively on the basis of claims 1 to 3 according to the first auxiliary request submitted at the oral proceedings and a description to be adapted.

Reasons for the Decision

1. The appeal is admissible.

Main request

2. Claim 1 of the main request meets the requirements of Article 123(2) EPC. The subject-matter of this claim is also new over the cited prior art; it differs in particular from the process of D1a by the presence of uranyl nitrate in the uranyl solution and from D2a by the absence of HF in the uranyl solution.

3. D1a represents the closest prior art. This document discloses a method for controlling the crystal grain size of UO_2 pellets comprising the step of reacting an aqueous uranyl fluoride solution with ammonia so as to precipitate ammonium diuranate (ADU), said solution being free from hydrofluoric acid and nitric acid, or not; calcining and reducing said ADU precipitate to form uranium dioxide powder; moulding and sintering said UO_2 powder to produce sintered pellets having a crystal grain size within the desired range of 10 to 100 µm. If HF is not present in the uranyl solution, the crystal grain size of the sintered pellets is controlled within the said range by adjusting the concentration of uranium in the uranyl fluoride

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solution between 50 and 1000 gU/liter, the crystal grain size of the sintered pellets decreasing as the uranium concentration increases (see page 1, claim 1; page 4, lines 10 to 35; page 7, Table 1; page 8, lines 15 to 21). In the examples, ammonia was added "quickly" to the uranyl fluoride solution. No value is given in D1a for the corresponding rate of addition. However, a comparison of the concentrations and grain sizes obtained in D1a, in the absence of HF (see Table 1), with those reported on page 8 of the present application and also obtained in the absence of HF and uranyl nitrate (see the four first lines of the Table) shows that in both cases sintered pellets with a crystal grain size falling within the range of 5-100 µm are obtained with uranium concentrations varying within the range 50-1000 gU/l. Furthermore, in the present application, which is from the same Applicant and inventors as D1a, a rate of addition of below 2 moles NH_3/min/mole U is said to be low and considered as practically unacceptable because of the resulting drastic decrease in the production rate of ADU. In these circumstances, it must be assumed that the "quick" addition of ammonia as taught in D1a corresponds to a rate of addition falling in the range of at least 2 moles NH_3/min/mole U, as also indicated in the decision under appeal and not contested by the Appellant.

3.1 The Appellant pointed out at the hearing that Table 1 of D1a showed that, in the absence of HF, an increase of the uranium concentration led to sintered pellets with the desired smaller crystal grain size but also caused a decrease of the sintered density well below 99% TD (99% of the theoretical density) when the concentration reached 500 gU/l and more. In the Appellant's view, the problem solved by the claimed process was to avoid this drawback and thus to control simultaneously the sintered density and the crystal

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grain size of the UO_2 pellets. In the statement of grounds of appeal, it was also emphasised in this context that controlling the crystal grain size whilst still obtaining a sintered density of at least 99% TD was an important technical effect of the invention.

The Board is not convinced that the problem stated above is solved by the process as defined in claim 1 of the main request. Claim 1 does contain the functional feature that the uranyl fluoride/uranyl nitrate ratio, the uranium concentration and the rate of contact between ammonia and the uranium components are adjusted within the indicated ranges so that UO_2 pellets having a predetermined crystal grain size of 5-100 µm are produced; however, it does not contain any limiting functional feature for the sintered density. Therefore, claim 1 encompasses a method of controlling the crystal grain size of UO_2 pellets within the range 5-100 µm, in which the sintered density may have any value, including values of 98% or lower. Furthermore, claim 1, when read in the light of the description, clearly embraces the alternative where the rate of addition of ammonia is adjusted at a predetermined value, for example the one disclosed in D1a (quick addition), the amount of uranyl nitrate present in the uranyl solution is very small, and the concentration of uranium is adjusted within the range of 50 to 1000 gU/l so as to produce pellets having a predetermined crystal grain size in the range from 5-100 µm. There is no evidence in the file that this alternative makes it possible to solve the problem stated above, and in view of the sintered density indicated in the Table of the present application and in Table 1 of D1a, the Board is not convinced that both a high sintered density of 99% TD and a small crystal grain size can be achieved by said alternative.

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3.2 Starting from D1a, the problem to be solved by the claimed process can be seen in providing an alternative process for controlling the crystal grain size of sintered UO_2 pellets within substantially the same range. In view of the data disclosed in the present application, it is credible that this problem is solved by the combination of features recited in the present claim 1.

3.3 This claim encompasses a method comprising the steps of adjusting the rate of addition of ammonia to the value used in D1a, adjusting the uranyl fluoride/uranyl nitrate ratio to a predetermined value and adjusting the uranium concentration between 50 and 1000 gU/l so as to produce UO_2 sintered pellets having a predetermined crystal grain size within the desired range. This method differs from the process of D1a in that an unspecified amount of uranyl fluoride is replaced by uranyl nitrate, or an unspecified amount of uranyl nitrate is added to the uranyl fluoride solution, as pointed out in the decision under appeal. D1a itself does not contain any information suggesting the addition of uranyl nitrate to the uranyl fluoride solution.

3.4 D2a, which concerns the manufacture of UO_2 nuclear fuel pellets for use in nuclear reactors, discloses that the formation of the ADU precipitate constitutes a critical step in this manufacture because the physical properties of the ADU precipitate can persist throughout the subsequent processing step of calcination-reduction to UO_2 (see D2a, page 123, left-hand column, last paragraph, and right-hand column, first paragraph). According to D2a, the ADU particles formed from a uranyl fluoride solution are much coarser than those formed from a uranyl nitrate solution at comparable concentration, and the ADU particle size distribution can be tailored to suit particular applications by adjusting the uranyl fluoride/uranyl nitrate ratio in the feed solution (see page 123, abstract; page 125, in particular Figure 4).

As D1a teaches that the properties of the sintered UO_2 pellets depend upon the properties of the calcined and reduced UO_2 powder, which in turn depend upon the properties of the original ADU precipitate, and recommends that the conditions of precipitation of the ADU be suitably controlled in order to control the crystal grain size of the UO_2 sintered pellets (see page 4, lines 7 to 35), the skilled person seeking an alternative process to D1a would have considered the teaching of D2a, although the latter does not mention the crystal grain size of the sintered pellets. In view of both documents, the skilled person would have expected that the addition of uranyl nitrate to the uranyl fluoride solution of D1a would provide a further possibility of controlling the ADU particle size and, thus, the crystal grain size of the sintered UO_2 pellets, namely by varying the uranyl fluoride/uranyl nitrate ratio in addition to the concentration of the uranium components. Therefore, the skilled person faced with the problem stated above would have contemplated adding uranyl nitrate to the uranyl fluoride solution of D1a (or replacing a part of the uranyl fluoride by uranyl nitrate) and varying the uranium concentration in the solution. Doing so, he would have arrived at the claimed solution.

3.5 Even if, as argued by the Appellant, the skilled person had expected the crystal grain size of the pellets to become larger, in view of D1a and D2a, by increasing the uranyl nitrate/uranyl fluoride ratio, he would not have been deterred from trying to add uranyl nitrate to the uranyl fluoride solution of D1a. In view of D1a, the skilled person also knew that the crystal grain size of the pellets is decreased by increasing the uranium concentration of the solution. Therefore, he would have expected the addition of uranyl nitrate in very small or in high amounts to the uranyl fluoride solution, combined with the variation of the uranium concentration, to be an alternative way for controlling the crystal grain size of the pellets in the desired range.

The Appellant's arguments concerning the presence of HF in the uranyl solution of D2a do not convince the Board that the skilled person would have refrained from testing the additional possibility of controlling the ADU particle size disclosed in D2a. There is no indication in D2a that the control of the ADU particle size distribution by adjustment of the uranyl fluoride/uranyl nitrate ratio can only be achieved when HF is present in the feed solution. Furthermore, the method for controlling the pellets' crystal grain size disclosed in D1a is not restricted to the use of uranyl fluoride solutions free from HF but also involves the use of solutions with a HF/UO_2F_2 in the range from 0 to 4:1. In these circumstances, the skilled person would have considered adding small amounts of uranyl nitrate in both alternatives of D1a, ie in the absence or in the presence of HF in the uranyl fluoride solution.

3.6 It follows from the above that the process according to claim 1 of the main request does not meet the requirement of inventive step set out in Articles 52(1) and 56. Therefore, the main request cannot be allowed.

Auxiliary request

4. The amendments in the claims of this request meet the requirements of Article 123(2) EPC. Claim 1 is based on claim 1 as originally filed, in which the possibility

of using a uranyl solution containing only one of the two uranyl components has been deleted. The sintered density of 99% TD is disclosed on page 9 of the original description (see table and last sentence on page 9), and the crystal grain size of "more than 20 µm" is implicitly derivable from the description, page 3, line 16, to page 4, line 2, and page 9. The adjustment of the uranium concentration and of the rate of contact of ammonia to "a predetermined value" within the indicated ranges is supported by the statement on page 6, lines 12 to 16, of the original description. The adjustment of the pellet crystal grain size to a desired value upwards by decreasing the relative amount of uranyl nitrate and/or increasing the rate of contact of ammonia or downwards by increasing the said amount of uranyl nitrate and/or decreasing the said rate of contact is directly and unambiguously derivable from the description as filed, page 7, lines 4 to 20, in combination with the Table bridging pages 8 and 9, and the two sentences on page 9. Claim 2 corresponds to original claim 2 and the preferred uranium concentration in claim 3 is disclosed on page 6, line 14, of the original description.

5. The claimed process also meets the requirement of novelty with respect to the cited prior art.

6. As indicated in point 3.1 above, the process of the closest prior art (D1a) has the drawback that, in the absence of HF in the uranyl fluoride solution, an increase of the uranium concentration in order to obtain pellets with smaller crystal grain sizes causes a decrease in the sintered density to values well below 99% TD (see Table 1 of D1a and also page 7 of the present application). Starting from D1a, the problem

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underlying the process defined in claim 1 was to provide a method for controlling the crystal grain size of sintered UO_2 pellets within the desired range of 20 to 100 µm while retaining the sintered density at the high level of 99% TD.

This problem is solved by the combination of features recited in claim 1. The claimed solution differs from the method of D1a in particular in that the uranyl fluoride solution also contains uranyl nitrate, and the crystal size of the pellets is adjusted to the desired value upwards by decreasing the relative amount of uranyl nitrate in the uranyl solution and/or increasing the rate of contact of the uranium components with ammonia or downwards by increasing the said amount of uranyl nitrate and/or decreasing the said rate of contact so as to produce sintered pellets having a predetermined grain size within the range of 20-100 µm and a sintered density of 99% TD. In view of the statements on pages 7 and 9 of the description and of the data in the Table bridging pages 8 and 9, which show in particular that the sintered density varies within the range of >98.8% to <9.3% TD when the crystal grain size of the pellets is decreased within the desired range by increasing the $UO_2(NO_3)_2/UO_2F_2$ ratio, the Board is satisfied that this problem has actually been solved by the claimed process. The said values for the sintered density are considered to be representative of the sintered density of 99% indicated in claim 1.

6.1 D1a itself does not contain any information which could point towards the claimed solution. As already stated above, D2a discloses that ADU particles formed from a uranyl fluoride solution are much coarser than those formed from a uranyl nitrate solution at comparable concentration, and that the ADU particle size distribution can be controlled by adjusting the uranyl fluoride/uranyl nitrate ratio in the feed solution. However, this document is completely silent as to the density of the resulting sintered UO_2 pellets. In these circumstances, the skilled person could not have expected in view of this teaching that the decrease of the sintered density of the pellets to values well below 99% TD might be avoided by adding uranyl nitrate to the uranyl fluoride solution of D1a and adjusting the ratio of these components to control the crystal grain size. In the absence of any expectation that the problem of **both** controlling the crystal particle size of the pellets within the desired range and retaining the sintered density at a high level of 99% TD might be solved by the disclosed addition of uranyl nitrate and variation of the uranyl fluoride/uranyl nitrate ratio, the skilled person would not have contemplated combining the teachings of D1a and D2a with a view to solving the technical problem mentioned above.

The alternative solution indicated in claim 1, which involves increasing (or decreasing) the rate of contact between the ammonia and the uranium components in the uranyl solution having a predetermined uranyl fluoride/uranyl nitrate ratio is also not suggested in either of D1a and D2a.

6.2 The remaining documents cited in the search report also do not contain information which could hint at the claimed solutions, when considered alone or in combination with the teaching of D1a and D2a.

6.3 It follows from the above that the subject-matter of claim 1 according to the first auxiliary request meets the requirement of inventive step set out in Articles 52(1) and 56 EPC.

7. Claim 1 being allowable, the same applies to dependent claims 2 and 3, whose patentability is supported by that of claim 1.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The case is remitted to the first instance with the order to grant a patent on the basis of claims 1 to 3 as filed at the oral proceedings and a description to be adapted.

The Registrar:

E. Görgmaier

The Chairman:

R. Spangenberg

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