

AUSTRALIA

Patents Act 1990

11002/92
641082

Patent Request/Notice of Entitlement

We, NORTON COMPANY, of 1 New Bond Street, Box Number 15008, Worcester, MA 01615-0008, United States of America, being the Applicant and Nominated Person, request the grant of a patent for an invention entitled:

"PROCESS FOR MANUFACTURING DISPERSIBLE BOEHMITE"

which is described in the accompanying standard complete specification.

Convention priority is claimed from the following basic application:

<u>Application Number</u>	<u>Country</u>	<u>Country Code</u>	<u>Date of Application</u>
07/673,873	United States of America	U.S.	22nd March 1991

The basic application was filed in the name of Ralph Bauer, who is the actual inventor of the invention. We have entitlement from the actual inventor, as well as from the applicant of the basic application, by assignment.

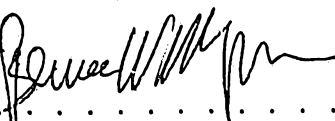
The basic application was the first application made in a Convention country in respect of the invention.

Our address for service is care of E. F. WELLINGTON & CO., Patent Attorneys, 312 St. Kilda Road, Melbourne, Victoria, 3004.

DATED this 17th day of February, 1992

For and on behalf of
NORTON COMPANY,

By:



BRUCE S. WELLINGTON

Patent Attorney for Applicant

To: The Commissioner of Patents,
Commonwealth of Australia
A/RR/982/1

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- (56) Prior Art Documents
EP 304721
US 4344928
US 4797139
- (57) Claim

1. A process for the production of a colloidal boehmite which comprises providing a starting material which is a dispersion of boehmite having a dispersibility (hereinbefore defined) of less than 70%, acidifying the dispersion to a pH of 3.5 or lower by adding acid in sufficient quantity to lower the pH to the above level but insufficient to cause the boehmite to dissolve completely, then subjecting the dispersion to a hydrothermal treatment by heating under a pressure of from 5 to 20 atmospheres at a temperature of from 150 to 200°C for a time of from 0.15 to 8 hours so as to produce a colloidal boehmite with a dispersibility (hereinbefore defined) of at least 90% and a lower Spot Index over the starting material.

7. A process for the production of a colloidal boehmite which comprises providing a starting material which is a dispersion of boehmite having a dispersibility (hereinbefore defined) of less than 70%, acidifying the dispersion to a pH of from 2 to 3 by adding acid in sufficient quantity to lower the pH to the above level but insufficient to cause the boehmite to dissolve completely, then subjecting the dispersion to a hydrothermal treatment

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by heating under an autogenous pressure of from 10 to 15 atmospheres at a temperature of from 160 to 180°C for a time of from ten minutes to 2 hours so as to produce a colloidal boehmite with a dispersibility (hereinbefore defined) of at least 95% and a Spot Index reduced to less than 50% of the figure obtained using the boehmite starting material.

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PATENTS ACT 1990

REGULATION 3.2

A-2391

64 1082

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Invention Title:

"PROCESS FOR MANUFACTURING DISPERSIBLE BOEHMITE"

Details of Associated Provisional Applications Nos:

The following statement is a full description of this invention
including the best method of performing it known to us.

BACKGROUND OF THE INVENTION

This invention relates to the manufacture of colloidal boehmite (sometimes called alpha alumina monohydrate) from less finely divided boehmite starting material.

5 In the production of ceramic forms of alumina with a very fine crystalline size of less than one micron, it is highly desirable to use as a starting material a similarly finely divided form of the precursor material. This is particularly true when the process used is a sol-gel process such as is
10 described in, for example US Patents 4,314,827 or 4,623,364. Such patents use a sol of alumina monohydrate which is then gelled either by reduction of water content or more usually by peptization using an acid. This gelled form may then be dried, comminuted and sintered at relatively low temperatures to give
15 alpha alumina structures with very fine and uniform particle sizes. The above process may be carried out in the presence of



modifying agents such as magnesia, zirconia, silica, titania, chromia or compounds that break down to such oxides under sintering conditions, and/or seed materials that favor the formation of the alpha alumina form. Such seed materials can be any one of those materials that are stable under the reaction conditions and which have the same crystal structure as the target alpha alumina and similar lattice parameters to those of alpha alumina. The preferred seed material is of course alpha alumina itself but other seed materials within the above definition such as alpha ferric oxide, added ab initio or generated in situ, can be used in many circumstances.

As indicated above it is highly advantageous in the operation of such a process that the boehmite dispersion be as fine as possible and as free as possible of agglomerates which tend to convert as such and produce similar agglomerates in the alpha form. It is found that such agglomerates are associated with a reduction in the properties of the final products. For example, abrasive grits made of such material are often less effective than those in which the crystal size is uniformly microcrystalline.

It is apparent therefore that there is substantial advantage in securing a feedstock that has the uniform microfine crystal structure referred to above. One method of obtaining such products is described in USP 4,117,105 in which an alumina

trihydrate is first calcined to increase its surface area through a partial dehydration and then autoclaved to achieve crystallization and rehydration. The result is apparently to produce a product with a crystallite size smaller than that of the starting material.

Another process for producing a water dispersible alumina from a hydrolysate of an aluminum alkoxide is described in USP 4,676,928. In this process the alumina slurry is aged at a pH of 5 to 9 at a temperature above 70°C for enough time to convert the greater part to a colloidal sol.

Other processes for the production of alumina in a sol form are described in US Patents 2,590,833; 2,787,522; 2,915,473; 3,357,791 and 3,966,893.

However none of the above methods are capable of converting an alumina monohydrate material having a substantial degree of particulate inhomogeneity into a product with essentially uniform, ultrafine, (ie less than 1000 angstroms), particles that are particularly suitable for the production of alpha alumina by a sol-gel route. The present invention provides



such a process and thus makes available to the maker of high grade alpha alumina products, or the catalyst monolith producer where alpha alumina is not required, a feedstock that had previously been unacceptable on account of the presence of agglomerated particles.

DESCRIPTION OF THE INVENTION

The present invention provides a process for the production of a colloidal boehmite which comprises providing a starting material which is a dispersion of boehmite having a dispersibility (hereinafter defined) or less than 70%, acidifying the dispersion to a pH of about 3.5 or lower by adding acid in sufficient quantity to lower the pH to the above level but insufficient to cause the boehmite to dissolve completely, then subjecting the dispersion to a hydrothermal treatment by heating under a pressure of from about 5 to about 20 atmospheres at a temperature of from about 150 to about 200°C for a time of from about 0.15 to about 8 hours so as to produce a colloidal boehmite with a dispersibility (hereinafter defined) of at least about 90% and a lower "Spot Index" over the starting material.



The dispersibility is defined as being the weight % of solids that cannot be centrifuged out of the dispersion by centrifuging in a polypropylene tube, (18mm x 100mm), at 3500G for 3 minutes. This property is therefore a measure of the presence of larger agglomerates in the material. The dispersibility is a guide to the quality of the final product that can be obtained from the boehmite by sintering. If a product with agglomerates is used, that is a product with a relatively low dispersibility, the final product will have a high "Spot Index". This parameter is measured by preparing abrasive grain with a size of 50 grit, (according to FEPA specifications), by the seeded sol-gel process described in USP 4,623,364. This grain is then mounted in an epoxy resin, and the grain surface is polished with a diamond powder. The polished surface is examined under visible light with a microscope at a magnification of 250x. The blemishes in each grain are then counted. After 50 grains have been counted, the spot index, (SI), is calculated from the following formula: $SI = 2(A+2B+3C+4D)$

where: A is the number of grains with 1-3 blemishes;

B is the number of grains with 4-6 blemishes;

C is the number of grains with 7-10 blemishes; and

D is the number of grains with 11 or more blemishes.

The Spot Index is therefore a direct indication of the number and size of agglomerates which appear in the final grain as blemishes.

An important feature of the present invention is that the thermal treatment is carried out at a pH of 3.5 or lower and preferably 3 or lower. As will be shown below, operation at higher pH values leads to poor dispersibility and a high spot index. Thus, while conversion to boehmite is efficiently achieved using the higher pH values described in prior art processes, the result is a boehmite with an excessive quantity of non-dispersible particles which are reflected in blemishes in any abrasive alpha alumina particles prepared therefrom.

The temperature at which the treatment is carried out is also significant. In general this temperature should be from about 150 to about 190°C and more preferably from about 160 to about 180°C. Since the higher temperatures tend to be more effective in reducing the Spot Index, temperatures in the upper halves of the above ranges are more preferred.

The heating is preferably conducted under autogenous pressure which conventionally reaches from about 10 to about 15 atmospheres. The pressure can of course be generated artificially if desired without changing the essential nature of the invention. Such pressure can range from about 5 to 20 atmospheres but preferably lies within the same range as autogenously generated pressure.

The time of the treatment is conveniently from about 10 to about 120 minutes. In general there is little benefit to be derived from a treatment longer than from about 30 to about 90 minutes at the treatment temperature.

5 The process of the invention can be carried out in the presence of other additives conferring specific advantages such as electrolytes for the control of viscosity and solids content; compounds that liberate a gas upon heating, (such as metal carbonates), if a porous end product is desired; modifiers such
10 as magnesia, zirconia, chromia and the like; grain growth inhibitors such as silica; and drying agents.

Of particular utility is the addition of seed material. Where the material treated is boehmite with a comparatively low dispersibility, it may often be advantageous to incorporate a
15 seed material that enhances the conversion of such boehmite to alpha alumina at lower temperatures. Such seed materials have the same crystal structure as alpha alumina with crystal lattice parameters that are close to those of alpha alumina. The best example is of course alpha alumina itself but other compounds
20 with close lattice parameter matches, such as alpha ferric oxide or a precursor of such a compound, can be used. The seed can be added before or after the hydrothermal treatment though addition before often makes the dispersion problem more tractable.

Where a seed material is present, it is important that it be present in a well dispersed, finely divided form. Seed particle sizes below one micron are in general preferred and particles less than 0.1 micron are even more preferred.

5 It is also within the scope of this invention to subject the boehmite having seed material incorporated therein, to a further process in which a sol of the treated boehmite is gelled and then formed, dried and fired to convert to alpha alumina. This corresponds to the processes described for
10 example in USPP 4,314,364; 4,623,364; 4,744,802; 4,964,883; (Jimmies); Published PCT Applications 90/08744 and 90/02160; and the like.

 The hydrothermal treatment of the invention can be carried out on a batch or a continuous basis and the water plus
15 boehmite can be subjected to a prior or subsequent deionization process if so desired.



Description of Preferred Embodiments

The invention is now further described with reference to the following examples which are for the purpose of illustration only and should not be interpreted as imposing any necessary limitation on the essential scope of the invention.

EXAMPLE 1

This Example illustrates the control over particle size and dispersibility by a treatment according to the invention.

Several test samples were given a hydrothermal treatment by placing 3.0g of Kaiser forming grade alumina monohydrate, (boehmite), in a large pyrex test tube along with 30ml of tap water and 1.2ml of 18 wt% of nitric acid, (enough to lower the pH of the mixture to below 3.5). The tubes were sealed by melting the end. Each tube was placed in a steel canister and placed in a pre-heated oven maintained at about 185°C +/- 5°C. The autogenous pressure is estimated at about 11 atmospheres.

As controls, the starting material was evaluated without the hydrothermal treatment and also with the hydrothermal treatment except for the exclusion of the acid.

It was found that, after 3 hours of acidified hydrothermal treatment, the initial powdery slurry had turned to a translucent gel filling the available liquid volume. There was no evidence of any of the original powder remaining. As time in the autoclave increased, the appearance of the gel gradually became more opaque and after 96 hours resembled dairy cream or a talcum powder dispersion.

The results are summarized in the following Table 1.

TABLE 1

Hours in Autoclave	Acid (+/-)	Dispersibility %	Ultimate Crystallite Size (A)*	Hardness after sintering ** (GPa)
Control				
0	-	30	64 +/- 1	<3
3	-	35	64 +/- 1	<3
0	+	30-35	64 +/- 1	<3
Evaluation				
1	+	39	75 +/- 1	ND
3	+	95	119 +/- 3	5-6
8	+	97	259 +/- 14	5-6
24	+	92	481 +/- 52	5-6
96	+	63	842 +/- 160	5-6

* Measured using an x-ray diffraction line broadening technique and the equation:

$$D = \frac{1.11 \times Y \times 57.3}{(B_{1/2} - b_{1/2}) \cos \frac{(2\theta)}{2}}$$

where: Y = CuK radiation = 1.54A

5 $b_{1/2}$ = width in degrees at half maximum of a reference
 material with crystallite size >3000A

$B_{1/2}$ = Width in degrees at half maximum of the sample
 of interest

20 = peak angle in degrees

10 57.3 = conversion factor radians/degrees

The 120 reflection was used in the measurement.

** Product sintered for 1 hour at 1400-1425°C

A Wilson Tukon microhardness tester, model LR, was used

15 As can be seen from the above, the presence of the acid
 significantly increased the dispersibility of the boehmite
 provided the time of treatment is not too prolonged. The
 particle size grew at a rate consistent with classical theory, ie
 as a function of the cube root of time. When the particles
 became very large there was a tendency to agglomeration and the
20 dispersibility decreased markedly.

EXAMPLE 2

This Example describes the result of subjecting a different alumina monohydrate to the hydrothermal treatment described in Example 1.

5 A sample of W.R. Grace SRA spray dried sludge SMR 14-1617 was given the hydrothermal treatment described in Example 1 for 3 hours at a temperature of 185°C except that 1.0g of magnesium nitrate were added to the mixture. Before treatment the dispersibility was 37% and afterwards it was 97%. The material, as received and before treatment, would not sinter to a
10 dense body whereas the treated product formed a translucent gel, dried to a rigid green form and sintered well to a hardness of 15 +/- 1 GPa, (>80% of theoretical).

EXAMPLE 3

15 This Example shows that the process of the invention is also effective with a seeded boehmite.

 An aluminum monohydrate (200g) available from Conoco under the trade name, Catapal, was mixed with 500ml of water in a waring blender for one minute. To the resulting slurry were
20 added 11.6g of an alpha alumina slurry containing 12.9% by weight of sub-micron alpha alumina.

Nitric acid was then added to the resultant slurry with stirring, in the form of an 13 wt% solution. A 100g sample was kept as a reference and the remainder was autoclaved in a PARR one litre model 4521 stainless steel autoclave equipped with a stirrer mechanism. The heat-up time was approximately 45 minutes and the time at the designated temperature is shown in the Table 2 below. After this the autoclave was switched off and cooled to ambient temperature over a period of about an hour. Upon cooling the samples were tested and the results appear in Table 2

TABLE 2

Temp. (°C)	pH	Ratio Acid/ Boehmite	Time (hr)	Dispersibility Before	Dispersibility After	Spot Index Before	Spot Index After	Hardness (GPa)
160	2	N.D.	0.5	94.9%	98.2%	400	205	20.3
160	2	N.D.	1.0	94.9%	98.0%	400	250	20.3
160	3	0.012	0.5	61.9%	95.9%	400		20.8
160	3	0.012	1.0	61.9%	95.5%	400	349	21.1
160	4	0.005	0.5	60.8%	54.1%	400	N.D.	<10.0
160	4	0.005	1.0	60.8%	53.8%	400	N.D.	<10.0
180	2	N.D.	0.5	94.9%	N.D.	400	16	20.6
180	3	0.012	0.5	61.9%	98.2%	400	6	20.6
180	4	0.005	0.5	60.8%	47.3%	400	N.D.	<10.0

Hardness was determined after sintering the hydrothermally treated sample at 1400°C in air for 5 minutes.

As can be readily seen from the above data increasing the amount of acid increases the initial dispersibility but that at lower levels of acid, (but still at a pH below 4), the initial low dispersibility can be improved by the hydrothermal treatment of the invention. In addition it is clear that increasing the temperature results in a highly beneficial improvement in the Spot Index. Finally, operation at pH of 4 resulted in a very low hardness in the final sintered product.

EXAMPLE 4

This Example follows the procedure of Example 3 except that a different boehmite is used.

The alumina monohydrate used was Versal 450, available from Kaiser Chemical Co. and made by neutralization of sodium aluminate liquor. In addition the seeding slurry was added in an amount of 23.2g. The results appear in Table 3.

TABLE 3

	Temp. (°C)	pH	Ratio Acid/ Boehmite	Time (hr)	Dispersibility		Spot Index		Hardness (GPa)
					Before	After	Before	After	
5	160	2	N.D.	0.5	44.7	71.5	>1000	N.D.	18.0
	160	2	N.D.	1.0	44.7	N.D.	>1000	38	17.4
	160	3	0.023	0.5	46.3	71.5	>1000	400	N.D.
	160	3	0.023	1.0	46.3	78.6	>1000	400	14.2
10	180	2	N.D.	0.5	44.7	98.8	>1000	21	19.0
	180	3	0.023	0.5	46.3	97.9	>1000	226	19.3
Control									
(No Autoclave)									
	--	3	0.023	--	46.3	--	>1000	--	<10

As will be apparent, the hydrothermal treatment markedly improves the dispersibility and the Spot Index very dramatically. In addition the sinterability, as indicated by the hardness, improves significantly as a result of the treatment.

EXAMPLE 5

This Example duplicates the procedure of Example 4 with the difference that acetic acid replaced nitric acid. Enough of the acid was added to bring the pH to 3.3 prior to autoclaving. After autoclaving for half an hour at 160°C, the Spot Index had declined from 400 to 106, whilst at 180°C the corresponding decline was from 400 to 9.

From the above Examples it can readily be appreciated that the process provides a most advantageous route to obtaining a boehmite with a greatly improved dispersibility at a relatively low cost. Because the boehmite starting material is a fluid slurry, sol or gel, dispersion of additives or seed materials in the boehmite starting material is easy. The process also offers the opportunity to control crystallite size in the final product.



The claims defining the invention are as follows:

1. A process for the production of a colloidal boehmite which comprises providing a starting material which is a dispersion of boehmite having a dispersibility (hereinbefore defined) of less than 70%, acidifying the dispersion to a pH of 3.5 or lower by adding acid in sufficient quantity to lower the pH to the above level but insufficient to cause the boehmite to dissolve completely, then subjecting the dispersion to a hydrothermal treatment by heating under a pressure of from 5 to 20 atmospheres at a temperature of from 150 to 200°C for a time of from 0.15 to 8 hours so as to produce a colloidal boehmite with a dispersibility (hereinbefore defined) of at least 90% and a lower Spot Index over the starting material.

2. A process according to Claim 1 in which the hydrothermal treatment is performed on a dispersion with a pH of 3 or lower.

3. A process according to Claim 1 in which the hydrothermal treatment is performed on a dispersion with a pH of from 2 to 3.

4. A process according to Claim 1 in which the hydrothermal treatment is conducted at a temperature of from 160 to 180°C.

5. A process according to Claim 1 in which the hydrothermal treatment is conducted under autogenous pressure.

6. A process according to Claim 1 in which the dispersibility of the colloidal boehmite after the hydrothermal treatment is at least 95%.



7. A process for the production of a colloidal boehmite which comprises providing a starting material which is a dispersion of boehmite having a dispersibility (hereinbefore defined) of less than 70%, acidifying the dispersion to a pH of from 2 to 3 by adding acid in sufficient quantity to lower the pH to the above level but insufficient to cause the boehmite to dissolve completely, then subjecting the dispersion to a hydrothermal treatment by heating under an autogenous pressure of from 10 to 15 atmospheres at a temperature of from 160 to 180°C for a time of from ten minutes to 2 hours so as to produce a colloidal boehmite with a dispersibility (hereinbefore defined) of at least 95% and a Spot Index reduced to less than 50% of the figure obtained using the boehmite starting material.

8. A process according to any one of Claims 1 to 7 in which the boehmite starting material comprises in addition a seed material effective to promote the formation of alpha alumina.

9. A process according to Claim 1 or 7, substantially as described herein with reference to any one of Examples 1-4.

10. A colloidal boehmite obtained by the process according to any one of Claims 1-9.

DATED this 22nd day of June, 1993

NORTON COMPANY,
By its Patent Attorneys,
E. F. WELLINGTON & CO.,
By:

BRUCE S. WELLINGTON



ABSTRACT

A boehmite or boehmite precursor can be improved in its dispersibility by subjecting it to a hydrothermal treatment at a pH of less than 3.5 and at elevated temperature and pressure.

