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(54) Titre : PROCÉDE POUR L'OBTENTION D'UN HYDROXYDE D'ALUMINIUM $Al(OH)_3$ EN FORME DE GRAINS
ARRONDIS

(54) Title: PROCESS FOR THE PRODUCTION OF AN ALUMINUM HYDROXIDE $Al(OH)_3$ HAVING ROUNDED GRAIN
SURFACES

(57) **Abrégé/Abstract:**

A process for the production of an aluminum hydroxide with rounded grain surfaces. An alkaline solution of a specific composition derived from the Bayer process is inoculated with an aluminum hydroxide with a specific grain distribution, followed by a step of precipitating aluminum hydroxide in particulate form. The aluminum hydroxide obtained according to the new process is especially suitable for the flameproof finishing of polyesters.

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ABSTRACT OF THE DISCLOSURE

A process for the production of an aluminum hydroxide with rounded grain surfaces. An alkaline solution of a specific composition derived from the Bayer process is inoculated with an aluminum hydroxide with a specific grain distribution, followed by a step of precipitating aluminum hydroxide in particulate form. The aluminum hydroxide obtained according to the new process is especially suitable for the flameproof finishing of polyesters.

This invention relates to a new process for the production of an aluminum hydroxide $[\text{Al}(\text{OH})_3]$ having rounded grain surfaces as well as flameproof plastic materials containing the $\text{Al}(\text{OH})_3$ as filler.

5 Aluminum hydroxide is a filler long known for flameproofing polymeric materials. The $\text{Al}(\text{OH})_3$ obtained from the Bayer process is mainly used as a filler either directly or optionally after a grinding process. However, the grain surfaces of these hydroxides are very irregular,
10 sharp-edged and fissured and, as a result, produce a rough surface on the correspondingly filled plastic molded articles.

In the incorporation of ground Bayer $\text{Al}(\text{OH})_3$ into plastic, unforeseeable viscosity variations have also been
15 observed that raise substantial problems in the manufacturing process. To counteract these difficulties, efforts have been made to coat the surface of the $\text{Al}(\text{OH})_3$ particles with silanes (German Patent No. 2,743,682). Besides the additional effort and the additional costs that
20 result from the separate coating, the processing properties of the so-treated $\text{Al}(\text{OH})_3$ are still unsatisfactory.

According to European Published Patent Application No. 011,667, it was then attempted to convert the $\text{Al}(\text{OH})_3$ resulting from the Bayer process (which is
25 present as agglomerates of individual crystals) in a heated aluminum subsaturated alkaline Bayer solution and to stir it for 1 to 25 hours, whereupon the solid material is separated. The original agglomerates are separated by this treatment at their grain boundaries. Thus, the individual
30 primary crystals undergo a rounding. Moreover, the resulting rounded $\text{Al}(\text{OH})_3$ particles have practically no fine-grain portion. This $\text{Al}(\text{OH})_3$ shows a very good viscosity behaviour in plastic materials, and moreover the resulting surfaces of the filled plastic molded articles
35 are smooth. However, a substantial drawback in this process is that contaminants contained in the original

Bayer $\text{Al}(\text{OH})_3$ are precipitated onto the resulting $\text{Al}(\text{OH})_3$, which leads to discoloration when using unsaturated polyester resins (UP resins).

It was proposed according to European Published Patent Application No. 407,595 that $\text{Al}(\text{OH})_3$ aggregates derived from the Bayer process be physically deagglomerated, e.g., by centrifugation or by grinding in a ball mill. However, damage to the grain surfaces occurs through the physical treatment which has a detrimental effect on the processing properties in the plastic. Moreover, such a treatment involves considerable expense.

A principal object of the invention is to provide a process that avoids the above-mentioned drawbacks of the known processes, and that produces $\text{Al}(\text{OH})_3$ which has rounded grain surfaces and excellent processing properties in plastics.

Accordingly one aspect of the invention provides a process for the production of aluminum hydroxide $\text{Al}(\text{OH})_3$ having rounded grain surfaces. In the process, an alkaline solution derived from the Bayer process, having a molar ratio of Na_2O to Al_2O_3 of from 2.0 to 2.3, is inoculated with an aluminum hydroxide, having a grain diameter in the 50 percent range d_{50} of 5 to 25 μm , in the 90 percent range d_{90} of 10 to 50 μm and in the 10 percent range d_{10} of 1.0 to 4.5 μm , and then with the resulting solid is precipitated and subsequently filtered off.

Preferably the aluminum hydroxide used for the inoculating or seeding is obtained by grinding and then grading an aluminum hydroxide derived from the Bayer process, having a grain diameter in the 50 percent range d_{50} of from 30 to 100 μm , and consisting of primary crystals having a grain diameter in the 50 percent range d_{50} of from 5 to 25 μm . Preferably the seed material is added to the alkaline solution at a temperature of from 60° to 75°C. Preferably the seed material is added to the alkaline solution in an amount of from 25 to 500 g/l. Preferably,

after seeding, the precipitation takes place until a molar ratio of Na_2O to Al_2O_3 of 2.6 to 3.1 has been reached.

The invention also provides a novel aluminum hydroxide having rounded grain surfaces with a grain diameter in the 50 percent range d_{50} of 5 to 25 μm , in the 90 percent range d_{90} of 10 to 50 μm , and in the 10 percent range d_{10} of 1.0 to 4.5 μm , a BET surface of 0.3 to 1.3 m^2/g , and a surface roughness coefficient of 1.1 to 1.5, which may be produced according to the process of the invention.

10 The invention further provides plastic materials, molding compounds and molded parts composed of polymeric materials which contain the aluminum hydroxide of the invention having rounded grain surfaces.

The invention further provides polymer
15 compositions containing the novel aluminum hydroxide as a flame-retarding filler and a process of preparing such compositions.

To obtain the $\text{Al}(\text{OH})_3$ used in the process according to the invention, an $\text{Al}(\text{OH})_3$ derived from the
20 Bayer process is ground in a manner which is known to those skilled in the art, e.g. in a ball mill, and graded with a suitable screening device.

This Bayer $\text{Al}(\text{OH})_3$ is originally available as an agglomerate with a particle size in the 50 percent range d_{50}
25 of 30 to 100 μm , usually of 50 to 70 μm . Correspondingly the primary crystals have a particle size in the 50 percent range d_{50} of 2 to 25 μm , suitably of 5 to 25 μm . The specific surface according to BET is suitably from 0.1 to 0.5 m^2/g , which results in a surface roughness of 2 to 6
30 (expressed as the quotient of the measured specific surface according to BET and the calculated surface based upon the assumption of an ideal ball shape for the particles).

The grinding and grading of the Bayer $\text{Al}(\text{OH})_3$ is carried out so that $\text{Al}(\text{OH})_3$ particles result which have the
35 following specifications:

Grain diameter in the 50 percent range d_{50} of 5 to 25 μm .
Grain diameter in the 10 percent range d_{10} of 1.0 to 4.5 μm .
Grain diameter in the 90 percent range d_{90} of 10 to 50 μm .
Specific surface, according to BET, of 1 to 3 m^2/g .

5 Surface roughness of 2 to 6.

An alkaline solution which is obtained from the Bayer process and which has a molar ratio of Na_2O to Al_2O_3 of from 2.0 to 2.3 is inoculated with this ground and graded $\text{Al}(\text{OH})_3$. An alkaline solution having a suitable composition can be obtained, for example, by mixing in equal parts a clear alkaline solution (K-solution) having a temperature of about 95°C , which is derived from the Bayer process and which has an Na_2O content of about 140 g/l and an Al_2O_3 content of 150 g/l, with a so-called P alkaline solution having a temperature of, e.g. 45°C , which was obtained after the crystallization of the $\text{Al}(\text{OH})_3$, and which has an Na_2O content of about 150 g/l and an Al_2O_3 content of about 85 g/l. Depending on the respective mixture ratio, the obtained alkaline solution has a temperature of from
10
15
20 45° to 95°C .

Preferably the seed material is added when the alkaline solution has a temperature of from 60° to 75°C .

The amount of seed material depends on the desired grain distribution in the desired product.
25 Suitably the seed material is used in an amount of from 25 to 500 g/l, preferably in an amount of from 50 to 150 g/l.

After the addition of the seed material, the suspension is precipitated, which can take place at constant temperature, by normal cooling or by cooling according to a specific temperature profile. Suitably the precipitation takes place up until a molar ratio of Na_2O to Al_2O_3 in the range of 2.6 to 3.1 has been reached. As a rule this process takes 24 to 60 hours. The suspension obtained after the precipitation is filtered in a manner
30
35 which is conventional to those skilled in the art.

The resultant $\text{Al}_2(\text{OH})_3$ is distinguished by the following properties:

- Grain diameter in the 50 percent range d_{50} of 5 to 25 μm .
Grain diameter in the 10 percent range d_{10} of 1.0 to 4.5 μm .
5 Grain diameter in the 90 percent range d_{90} of 10 to 50 μm .
Specific surface, according to BET, of 0.3 to 1.3 m^2/g .
Surface roughness of 1.1 to 1.5.

Because of its excellent viscosity behaviour, this $\text{Al}_2(\text{OH})_3$ produced according to the process of the
10 invention can be worked problem-free into plastics, preferably into thermosetting plastics, such as unsaturated polyester resins (UP resins). Extraordinarily high filling ratios of filled plastics with very good property profiles can be thus achieved. The surfaces of suitably produced
15 molded articles are smooth.

The following Examples illustrate the invention.

Example 1

A P-alkaline solution at 45°C with an Na_2O content of 145 g/l and an Al_2O_3 content of 88 g/l was mixed in an
20 agitation decomposer (8 m^3 capacity) with a K-alkaline solution at 75°C with an Na_2O content of 139 g/l and an Al_2O_3 content of 155 g/l. 5 m^3 of a mixed alkaline solution with a molar ratio of Na_2O to Al_2O_3 of 2.01 resulted. This mixed alkaline solution was heated to approximately 70°C and
25 mixed with 50 kg/m^3 of a ground Bayer $\text{Al}(\text{OH})_3$ with d_{50} of 9 to 13 μm , d_{10} of 1.5 μm , d_{90} of 19 μm and a specific surface according to BET of 2.21 m^2/g as the seed material. The resulting temperature was 67°C. The precipitation process was now carried out according to the following temperature
30 profile: cooled from 67° to 60°C over 12 hours and then stirred for 36 hours at this temperature. After this precipitation time, a molar ratio of Na_2O to Al_2O_3 of 2.96 was reached, which corresponded to an Al_2O_3 yield of 37 kg/m^3 . The total product yield (including the amount of
35 seed material) of this absorptive precipitation process was 540 kg of aluminum hydroxide. The precipitated suspension

was filtered on a band filter (approximately 15 m² filter surface) and the moist aluminum hydroxide was dried on a contact drier. The resultant Al(OH)₃ had a grain diameter in the 50 percent range of 8.7 μm, in the 10 percent range of 1.6 μm and in the 90 percent range of 19 μm, a specific surface according to BET of 1.18 m²/g and a surface roughness of 1.31. The viscosity of each of (a) the initial product, (b) the Al(OH)₃ according to the invention which was obtained according to Example 1 and (c) a product which was obtained according to the process of European Published Patent Application No. 011,667 (Apyral 4 of Vereinigte Aluminum Werke) for comparison, was tested in an acrylic resin (Modar 826 HT, ICI Acrylix).

Measurement conditions: 170 parts of Al(OH)₃ per 100 parts of resin, Brookfield HBT viscosimeter, Spindel 2, 50 rpm, 20°C

The following viscosities were measured:
(a) 4000 mPaS (starting material).
(b) 2400 mPaS (invention).
(c) 2600 mPaS (comparison).

A comparison of the degree of whiteness between product (b) and product (c), measured according to DIN 53163 (Erepho, 475 nm, Standard BaSO₄), was as follows:
(b) 91.0 percent (invention).
(c) 86.2 percent (comparison).

Example 2

A P-alkaline solution at 48°C with an Na₂O content of 152 g/l and an Al₂O₃ content of 78 g/l was mixed in an agitation decomposer (8 m³ capacity) with a K-alkaline solution at 82°C with an Na₂O content of 144 g/l and an Al₂O₃ content of 164 g/l. 5 m³ of a mixed alkaline solution with a molar ratio of Na₂O to Al₂O₃ of 2.02 resulted. This mixed alkaline solution was heated to approximately 63°C and mixed with 150 kg/m³ of a ground Bayer Al(OH)₃ with d₅₀ of 9 to 13 μm, d₁₀ of 15 μm and d₉₀ of 19 μm and a specific surface

according to BET of $2.21 \text{ m}^2/\text{g}$ as the seed material. The resulting temperature was 60°C . The precipitation process was operated at a steady temperature of 60°C for 48 hours. After this precipitation time, a molar ratio of Na_2O to Al_2O_3 of 3.1 was reacted, corresponding to an Al_2O_3 yield of 37 kg/m^3 . The total product yield of this precipitation process (including the seed material amount) was 1063 kg of aluminum hydroxide. The precipitated suspension was filtered on a band filter (approximately 15 m^2 filter surface) and the moist aluminum hydroxide was dried on a contact drier. The resultant $\text{Al}(\text{OH})_3$ had a grain diameter in the 50 percent range of $6.8 \text{ }\mu\text{m}$, in the 10 percent range of $1.5 \text{ }\mu\text{m}$, and in the 90 percent range of $15 \text{ }\mu\text{m}$, a specific surface according to BET of $1.21 \text{ m}^2/\text{g}$ and a surface roughness of 1.2. The viscosity was measured by the same method described in Example 1 and the results were:

- (a) 4000 mPaS (starting material).
- (b) 1600 mPaS (invention).
- (c) 2600 mPaS (comparison).

Example 3

A P-alkaline solution at 42°C with an Na_2O content of 148 g/l and an Al_2O_3 content of 101 g/l was mixed in a laboratory agitation decomposer (10 l capacity) with a K-alkaline solution at 79°C with an Na_2O content of 138 g/l and an Al_2O_3 content of 154 g/l. 8 l of a mixed alkaline solution with a molar ratio of Na_2O to Al_2O_3 of 2.04 resulted. This mixed alkaline solution was heated to about 70°C and mixed with 100 g/l of a ground Bayer $\text{Al}(\text{OH})_3$ with d_{50} of $8.26 \text{ }\mu\text{m}$, d_{10} of $1.41 \text{ }\mu\text{m}$ and d_{90} of $19.8 \text{ }\mu\text{m}$, a specific surface according to BET of $2.03 \text{ m}^2/\text{g}$ and a surface roughness of 2.44 as the seed material. The resulting temperature was 67°C . The precipitation process was then operated according to the following temperature profile: cooled to 60°C over 24 hours and then stirred for 26 hours at this temperature. After this precipitation time, a

molar ratio of Na_2O to Al_2O_3 of 2.78 was reached, corresponding to an Al_2O_3 yield of 33.5 kg/m^3 . The total product yield (including the seed material amount) was 1.21 kg of aluminum hydroxide. The precipitated suspension was
5 filtered on a laboratory nutsch filter (about 500 m^2) and dried in a drying oven at 105°C . The resultant $\text{Al}(\text{OH})_3$ had a grain diameter in the 50 percent range of $8.14 \mu\text{m}$, in the 10 percent range of $1.6 \mu\text{m}$ and in the 90 percent range of $19.6 \mu\text{m}$, a specific surface according to BET of $0.89 \text{ m}^2/\text{g}$
10 and a surface roughness of 1.21. The viscosity of each of the initial product (a) and of product (b) obtained according to Example 3 were tested in an unsaturated polyester resin (Synolite W20, DSM).

Measurement conditions: 175 parts of $\text{Al}(\text{OH})_3$ per 100 parts
15 of resin, Brookfield HBT viscosimeter,
Spindel 3, 5 rpm, 23°C

The measured viscosities were as follows:

(a) 141.6 PaS
20 (b) 57.3 PaS .

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the production of aluminum hydroxide, $\text{Al}(\text{OH})_3$, having rounded grain surfaces, which comprises inoculating an alkaline solution derived from the Bayer process and having a molar ratio of Na_2O to Al_2O_3 of from 2.0 to 2.3, with an aluminum hydroxide having grain diameter characteristics in the 50 percent range d_{50} of 5 to 25 μm , in the 90 percent range d_{90} of 10 to 50 μm and in the 10 percent range d_{10} of 1.0 to 4.5 μm , and then precipitating and filtering off the resultant solid.

2. A process according to claim 1, wherein the aluminum hydroxide used for the inoculating is obtained by grinding and then grading an aluminum hydroxide derived from the Bayer process, having a grain diameter in the 50 percent d_{50} of 30 to 100 μm , and consisting of primary crystals having a grain diameter in the 50 percent range of 5 to 25 μm .

3. A process according to claim 1 or 2, wherein the inoculating material is added to the alkaline solution at a temperature of from 60° to 75°C.

4. A process according to claim 3, wherein the inoculating material is added in an amount of from 25 to 500 g/l.

5. A process according to claim 1, 2 or 4, wherein the precipitation takes place until a molar ratio of Na_2O to Al_2O_3 of 2.6 to 3.1 has been reached.

6. An aluminum hydroxide with rounded grain surfaces and a grain diameter in the 50 percent range d_{50} of 5 to 25 μm , in the 90 percent range d_{90} of 10 to 50 μm , and in the 10 percent range d_{10} of 1.0 to 4.5 μm , a BET surface

of 0.3 to 1.3 m²/g, and a surface roughness coefficient of 1.1 to 1.5.

7. An aluminum hydroxide with rounded grain surfaces and a grain diameter in the 50 percent range d_{50} of 5 to 25 μm , in the 90 percent range d_{90} of 10 to 50 μm , and in the 10 percent range d_{10} of 1.0 to 4.5 μm , a BET surface of 0.3 to 1.3 m²/g, and a surface roughness coefficient of 1.1 to 1.5, when produced according to the process of claim 1, 2 or 4.

8. A plastic material, a molding compound or a molded part composed of polymeric material, which contains the aluminum hydroxide having rounded grain surfaces as defined in claim 6.

9. A flame-retardant polymeric composition comprising a polymeric material which contains the aluminum hydroxide having rounded grain surfaces as defined in claim 6, as a flame-retarding filler.

10. A process of preparing a flame-retardant polymeric composition, comprising incorporation into a polymeric material the aluminum hydroxide having rounded grain surfaces as defined in claim 6, as a flame-retarding filler.