Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2097934 C 2002/04/09

(11)(21) 2 097 934

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 1991/11/28
(87) Date publication PCT/PCT Publication Date: 1992/06/25
(45) Date de délivrance/Issue Date: 2002/04/09
(85) Entrée phase nationale/National Entry: 1993/06/07
(86) N° demande PCT/PCT Application No.: EP 1991/002251
(87) N° publication PCT/PCT Publication No.: 1992/010426
(30) Priorité/Priority: 1990/12/07 (P 40 39 053.5) DE

(51) Cl.Int.^{5}/Int.Cl.^{5} C01F 7/14

(72) Inventeurs/Inventors:
Foell, Juergen, DE;
Bunte, Reinhard, DE;
Hachgenei, Johannes, DE

(73) Propriétaire/Owner:
HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN, DE

(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : UTILISATION DE POLYGLYCERINES DANS LE PROCEDE DE BAYER POUR ACCROITRE LA TAILLE CRYSTALLINE DE CE PRODUIT

(54) Title: USING POLYGLYCERINES IN THE BAYER PROCESS TO INCREASE CRYSTAL SIZE OF THE PRODUCT

(57) Abrégé/Abstract:
The invention concerns the production of aluminium oxide trihydrate crystals by the bayer process by digesting ground bauxite, filtering off the red mud, cooling the filtrate and crystallizing out the dissolved aluminium hydroxide as gibbsite. Before and/or during the crystallization, polyglycerins of the general formula: H-($OCH_2CHOH-CH_2$)$_n$-OH are added, n being a whole number greater than or equal to 3.

C01F

(21) Int. Application Number: PCT/EP91/02251
(22) Int. Filing Date: 28 November 1991 (28.11.91)
(30) Priority data:
P 40 39 053.5 7 December 1990 (07.12.90) DE
(51) International Patent Classification 5 : C01F 7/14
A1
(11) Int. Publication Number: WO 92/10426
(43) Int. Publication Date: 25 June 1992 (25.06.92)

(54) Title: POLYGLYCERINS IN THE BAYER PROCESS

(71) Applicant (for all designated States except US): HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE]; Henkelstraße 67, D-4000 Düsseldorf 13 (DE).

(72) Inventors; and
(75) Inventors/Applicants (for US only) : HACHGENEI, Johannes [DE/DE]; Hospitalstraße 18, D-4000 Düsseldorf 13 (DE). BUNTE, Reinhard [DE/DE]; Bismarckstraße 30, D-4047 Dormagen 11 (DE). FÖLL, Jürgen [DE/DE]; Nosenbergerstraße 34, D-4000 Düsseldorf 30 (DE).

(74) Common Representative: HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN; TFP-Patentabteilung, Henkelstraße 67, D-4000 Düsseldorf 13 (DE).

(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent), US.

Published
With international search report.

(57) Abstract

The invention concerns the production of aluminium oxide trihydrate crystals by the bayer process by digesting ground bauxite, filtering off the red mud, cooling the filtrate and crystallizing out the dissolved aluminium hydroxide as gibbsite. Before and/or during the crystallization, polyglycerins of the general formula: $H-(OCH_2CHOH-CH_2)_n-OH$ are added, n being a whole number greater than or equal to 3.

C02F

(21) Int. Application Number: PCT/SU90/00272
(22) Int. Filing Date: 7 December 1990 (07.12.90)
(51) International Patent Classification 5 : C02F 1/28
A1
(11) Int. Publication Number: WO 92/10427
(43) Int. Publication Date: 25 June 1992 (25.06.92)

(54) Title: METHOD OF WATER PURIFICATION

(71)(72) Applicant and Inventor: FOMINSKY, Leonid Pavlovich [SU/SU]; ul. Yaroslavskaya, 8-212, Cherkassy, 257010 (SU).

(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US.

Published
With international search report.

(57) Abstract

A method of water purification provides for introducing into the water a sorbent-suspension obtained by electroerosive dispersion of ferrous metals in the water and containing no more than 3 % of magnetite, mixing and subsequent separation of the solid phase. The suspension is fed into the water at a quantity of 3 to 120 g of dry substance for 1 g of impurities. Mixing of the suspension with the water is effected at a temperature of 20-70 °C.

USING POLYGLYCERINES IN THE BAYER PROCESS TO INCREASE CRYSTAL SIZE OF THE PRODUCT

This invention relates to a process for the production of an aluminium oxide trihydrate crystallizate by the Bayer process.

The Bayer process is a process for obtaining aluminium hydroxide from bauxite (**Büchner, Schliebs, Sinter, Büchel, Industrielle anorganische Chemie, VCH Weinheim 1984, pages 259 and 260; Ullmanns Encyklopädie der technischen Chemie, 4th Edition, Vol. 7, VCH Weinheim 1982, pages 305 et seq.**). The process comprises the following main steps:

- ground bauxite is digested with aqueous sodium hydroxide in an autoclave at temperatures of 140 to 200°C to form soluble sodium aluminate,
- iron-containing red sludge is separated off,
- the filtrate oversaturated with aluminium hydroxide is slowly cooled with stirring and inoculated with a large quantity of aluminium hydroxide ("stirring-out"), a large part of the dissolved aluminium hydroxide accumulating as hydrargillite,
- the aluminium hydroxide thus obtained is filtered off and the liquor substantially freed from aluminium hydroxide is returned to the process.

Crystallization of the aluminium hydroxide is kinetically inhibited to a considerable extent so that the precipitation phase is carried out with a gradual reduction in temperature, for example to 10°C, over a period of 24 to 48 h during which a large quantity of crystal nuclei is added. In addition to crystallization

of the aluminium hydroxide, the agglomeration of fine particles to build up relatively large crystal agglomerates is of considerable importance during the stirring-out process. Most of the aluminium hydroxide thus obtained is then calcined to aluminium oxide in another process step.

According to **Aluminiumtaschenbuch, 14th Edition, 1988, page 11**, by far the largest part of the oxide produced is processed to metal in aluminium works. A relatively small proportion, including the hydroxide form, is used for various applications in chemistry, ceramics and other fields. The metallurgical oxide has to meet particularly stringent requirements. A moderately calcined oxide having an alpha-Al_2O_3 content of less 30% and very few fines smaller than 45 μm in size is particularly preferred. Because of this requirement, stringent demands are imposed on the crystallization process which can be influenced by impurities in the crystallization solution. The impurities in question are, above all, the salts of huminic acids and degradation products thereof, such as sodium oxalate (see **DE-A-36 09 662**). Sodium oxalate is particularly troublesome because it shows similar crystallization behavior to aluminium hydroxide and can even act as a crystallization nucleus. This leads on the one hand to a less pure hydroxide and, on the other hand, to distinctly smaller crystals.

Numerous efforts have been made in the prior art to improve the crystallization of aluminium hydroxide in order to obtain coarser crystals.

US-A-4,608,237 (DE-A-36 09 662) describes the use of polymers or copolymers of acrylic or methacrylic acid derivatives to influence the crystallization of aluminium hydroxide. **US-A-4,737,352** describes the use of fatty acids in an oil carrier in the Bayer process which is

said to give coarser crystals.

It is known from **Chemical Abstracts 92 (12), Abstract 96203s**, that glycerol distinctly inhibits the crystallization of aluminium hydroxide.

Against this background, the problem addressed by the present invention was to improve the known process for the formation of aluminium oxide trihydrate crystallizate by the Bayer process to the extent that new crystallization aids would be made available for precipitation of the aluminium hydroxide.

It has surprisingly been found that, even in relatively low concentrations in the crystallization liquor, polyglycerols lead to an aluminium hydroxide precipitate having a distinctly coarser degree of crystallinity compared with the prior art.

In a first embodiment, therefore, the present invention relates to a process for the formation of an aluminium oxide trihydrate crystallizate by the Bayer process by

- digestion of crushed bauxite
- removal of the red mud
- cooling of the filtrate and
- crystallization of the dissolved aluminium hydroxide as hydrargillite,

characterized in that polyglycerols corresponding to general formula (I)

$$H-(OCH_2CHOH-CH_2)_n-OH \qquad (I)$$

in which n is an integer of, or greater than, 3, are added before and/or during the crystallization phase.

The polyglycerols are polyethers having permanent OH functions which are obtained by alkali-catalyzed condensation of glycerol (see, for example, **Ullmanns**

Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A12, pages 487-489). As normal in polycondensation reactions, a more or less broad distribution of polymer rather than a certain homolog in pure form is obtained. In this sense, the polyglycerols to be used in accordance with the invention are not individual defined condensation products, in which the index n stands for a certain number, but instead are mixtures of condensation products in which the index "n" indicates the statistical distribution of the polyglycerols present. According to **Ullmanns Encyclopädie der technischen Chemie, 4th Edition, Vol. 12, page 374**, polyglycerols have relative molecular weights of 166 (6 carbon atoms) to 2238 (90 carbon atoms) and 4 to 32 hydroxyl groups. Although, theoretically, infinitely long polymer chains can be produced, the polycondensation reaction generally stops at shorter chain lengths so that, hitherto, chain lengths below n = 50 only have been reported. Since the viscosity of the polyglycerols generally increases with increasing chain length so that their handling properties deteriorate, a preferred embodiment of the present invention is characterized by the use of polyglycerols corresponding to general formula (I) in which n is a number of 3 to 30. By virtue of their lower viscosity, the relatively short-chain polyglycerols are preferred for the purposes of the invention.

In the same way as monoglycerol itself, diglycerol gives unacceptable particle size distributions, more particularly crystallizates having a very high percentage of fines. It is assumed that commercially available diglycerol still contains certain amounts of monoglycerol which inhibits the crystallization of aluminium hydroxide. However, it may be assumed that, with increasing degree of condensation, the percentage content of monoglycerol decreases as, hence, does the

crystallization inhibiting effect. However, this effect is counteracted by the increased viscosity of the polyglycerols with increasing chain length so that particularly preferred polyglycerols for the purposes of the invention consist of 3 to 12 glycerol units.

Basically, the quantity of polyglycerols (I) to be used is not critical, but is determined by the technical requirements which the desired crystallizate is expected to satisfy. A small quantity of polyglycerols corresponding to general formula (I) does not of course influence the crystallization process whereas an excessive quantity of polyglycerols corresponding to general formula (I) on the one hand can lead to a certain contamination of the aluminium hydroxide, but should be avoided on an industrial scale, particularly from the point of view of the economy of the precipitation process, especially when the extremely large conversions are taken into consideration.

Accordingly, one preferred embodiment of the process according to the invention is characterized in that polyglycerols corresponding to general formula (I) are added to the filtrate of the Bayer process in a quantity of 0.01 to 5 g/l. In another preferred embodiment, 0.05 to 2 g/l of the polyglycerols corresponding to general formula (I) is added to the filtrate of the Bayer process.

According to the present invention, any other crystallization aid known from the prior art in addition to the polyglycerols corresponding to general formula (I) may also be used in principle to precipitate aluminium hydroxide. Examples of known crystallization aids are the high molecular weight acrylic or methacrylic acid polymers or copolymers mentioned above or the above-mentioned fatty acids in an oil carrier.

The invention is illustrated by the following

Examples.

Examples and Comparison Examples

The following Examples and Comparison Examples for studying the influence of the crystallization aids were carried out using controlled liquors from a Bayer process. The liquors had compositions which also occur in industrial processes:

197.3 g/l of $Al(OH)_3$ = 129 g/l of Al_2O_3
45.6 g/l of Na_2CO_3
278.0 g/l of NaOH, 50%, corresponds to 108 g/l Na_2O, 184 g/l Na_2CO_3.

These solutions are also characterized by the following data:

Quantitative ratio of $Na_2O:Al_2O_3$: 1.37
TC (total caustic, free alkalinity): 184 g/l of Na_2CO_3
TA (total alkali, total alkalinity): 230 g/l of Na_2CO_3
Al_2O_3/TC: 0.70.

400 ml of this solution were introduced hot into a double-jacketed spherical flask and, after addition of the particular crystallization aid, were cooled with vigorous stirring from 78° C to 71° C over a period of 21 h. The crystalline $Al(OH)_3$ obtained was then filtered off, repeatedly washed and dried **in vacuo** at 100° C. In all the examples, the yield of crystalline $Al(OH_3)$ was about 30 g, except when glycerine (0.5 g to 400 ml) was added, when a yield of 6 g was obtained. The crystal size distribution was determined by sieving.

The following Table illustrates the superiority of the crystallization aids to be used in accordance with the invention to the prior art in Examples 1 to 6

and Comparison Examples 1 to 3 which were each based on the procedure described above.

Table

Ex.	Degree of polycondensation of polycerol (n)	Quantity of polyglycerol in g/400 ml	Percentages by weight of $Al(OH)_3$ crystals <150µm	<100µm	<75µm	<45µm
1	5	0.5	36	1	0.3	-
2	5	0.1	41	3	2	1
3	5	0.05	52	2	2	1
4	5	0.02	70	16	14	8
5	10	0.5	56	7	6	4
6	10	0.1	69	8	7	4
Comp. 1	-	-	93	21	17	1
Comp. 2	1	0.5	96	95	92	31
Comp. 3	2	0.5	69	36	35	20

The above Table shows that even the addition of small quantities of polyglycerols corresponding to general formula (I) to the aluminate liquor leads to a distinct increase in the size of the crystals obtained whereas the addition of glycerol (Comparison Example 2) and diglycerol (Comparison Example 3) leads to only a slight increase in the size of the crystals obtained in relation to Comparison Example 1 where no crystallization aid is added.

The percentages by weight in % by weight in the Table are not standardized to 100% by weight because the sum total of the respective percentages which is smaller than the corresponding size is shown.

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

1. A process for the formation of aluminum oxide trihydrate crystals, said process comprising the steps of:

- digestion of crushed bauxite
- removal of the red mud
- cooling of the filtrate and
- crystallization of the dissolved aluminum hydroxide as gibbsite,

wherein the improvement comprises adding polyglycerines corresponding to the general formula (I)

$$H-(OCH_2CHOH-CH_2)_n-OH \qquad (I)$$

in which n is an integer equal to or greater than 3, to the crystallization liquor before, during, or both before and during, the crystallization in an amount sufficient to increase the average size of the gibbsite crystals produced in the process.

2. A process as claimed in claim 1, wherein the polyglycerines are selected from the group consisting of those corresponding to general formula (I), when n is a number of 3 to 30.

3. A process as claimed in claim 2, wherein the polyglycerines are selected from the group consisting of those corresponding to general formula (I), when n is a number of 3 to 12.

4. A process as claimed in claim 2, wherein the polyglycerines corresponding to general formula (I) are added to the crystallization liquor in a quantity of 0.01 to 5 g/l.

5. A process as claimed in claim 4, wherein the polyglycerines corresponding to general formula (I) are added to the crystallization liquor in a quantity of 0.05 to 2 g/l.

6. A process as claimed in claim 1, wherein the polyglycerines corresponding to general formula (I) are added to the crystallization liquor in a quantity of 0.01 to 5 g/l.

7. A process as claimed in claim 6, wherein the polyglycerines corresponding to general formula (I) are added to the crystallization liquor in a quantity of 0.05 to 2 g/l.