

The present invention concerns the preparation of stable aqueous suspensions of ^{amorphous} silico-aluminate and the use thereof in the paper-making industry.

Aqueous suspensions or slurries of silico-aluminates are used in a number of fields, in particular in the paper-making industry.

Now, those suspensions have a tendency to undergo sedimentation or gelling, which makes it difficult for them to be transported or stored. Indeed, in very many cases, following transportation of the suspension or after storage thereof over a period of greater or lesser length, the deposit of a hard layer of pigment above which is a slurry which is more fluid but which has a low content of dry matter is observed. It is also often impossible to put the silico-aluminate back into a state of suspension or to produce a slurry which is of sufficiently low viscosity to be pumpable and therefore capable of use in an industrial content. That therefore involves a certain problem.

It has been envisaged that aqueous suspensions of certain crystalline synthetic silico-aluminates may be stabilised: EP-A-0154291 describes aqueous suspensions of zeolite which are stabilised by xanthane gum; EP-A-0233689 proposes stabilising aqueous dispersions of zeolite by the addition of a lipopolysaccharide produced by a microorganism belonging to the species Acinetobacter.

The main subject-matter of the invention is therefore a suspension of amorphous silico-aluminate which is stable, pumpable and dispersible after several days storage.

For that purpose the stable aqueous suspension according to the invention is characterised in that it comprises a synthetic amorphous silico-aluminate and, as a stabilising agent, a biogum.

It has been found that after storage for several days, the suspensions of the invention exhibited no or only little sedimentation and in every case remained of suitable viscosity.

Other features and advantages of the invention will be better

appreciated from the following description and specific but non-limiting examples.

In accordance with a particular embodiment of the invention the suspension is based on an alkali metal silico-aluminate, in particular of sodium.

In the latter case, products of the following formula may be mentioned:



$$x = 0.1 \text{ to } 2; y = 1.5 \text{ to } 16; w = 0.3 \text{ to } 4.$$

The synthetic amorphous silico-aluminates which are suitable for use in accordance with the invention may be produced by any known method which however does not fall within the scope of the invention. Generally, the operating procedure involves neutralisation of a silicate with an aluminium salt, in particular aluminium sulphate, or an aluminate.

In accordance with a preferred embodiment of the invention the suspension is based on a silico-aluminate produced by precipitation and formed by a filter cake which results from the precipitation reaction and which is slaked.

In other words, precipitation of the silico-aluminate is effected in particular by reaction of a silicate with aluminium sulphate or an aluminate, as has been indicated hereinbefore. The reaction medium is then filtered and the result obtained is a filter cake which is washed if necessary. The cake is then slaked, thus forming a suspension which, in the embodiment referred to herein, constitutes the suspension of the invention which is stabilised by the means described hereinafter.

It may also be noted that it is possible to add to that suspension dry silico-aluminate, in particular in powder form, so as to

increase the amount of dry matter in the suspension.

The stabilising agent used is a biogum.

Biogums are polysaccharides of high molecular weight which is generally higher than one million, produced by fermentation of a carbohydrate under the action of a microorganism.

Biogums that may be mentioned as being suitable for use in the suspension in accordance with the present invention include those produced by fermentation under the action of bacteria or fungi belonging to the genus Xanthomonas such as Xanthomonas begoniae, Xanthomonas campestris, Xanthomonas carotae, Xanthomonas hederae, Xanthomonas incanae, Xanthomonas malvacearum, Xanthomonas papavericola, Xanthomonas phaseoli, Xanthomonas pisi, Xanthomonas vasculorum, Xanthomonas vesicatoria, Xanthomonas vitians and Xanthomonas pelargonii; the genus Arthrobacter and more particularly the species Arthrobacter stabilis and Arthrobacter viscosus; the genus Erwinia; the genus Azotobacter and more particularly the species Azotobacter indicus; the genus Agrobacter and more particularly the species Agrobacterium radiobacter, Agrobacterium rhizogenes and Agrobacter tumefaciens; the genus Alcaligenes and more particularly the species Alcaligenes faecalis; the genus Rhizobium; the genus Sclerotium and more particularly the species Sclerotium rolfsii and Sclerotium glucanicum; the genus Corticium; the genus Sclerotinia; and the genus Stromatinia.

The biogum to be used, which can be produced by fermentation by means of the above-described microorganisms, is more particularly the gum produced by fermentation of bacteria of the genus Xanthomonas.

It will be appreciated that the use of a mixture of biogums as a stabilising agent would not be a departure from the scope of the present invention.

It is advantageous to use an anti-bacterial agent of the type comprising for example sodium benzoate, glutaraldehyde and formaldehyde,

in combination with the biogum.

The biogum is generally used in an amount which varies between 0.05% and 5% by weight with respect to the dry matter and more particularly between 0.1 and 1%.

- 5 The proportion of dry matter in the suspension is usually at least 15%, preferably at least 25%. The amount of aluminium expressed as Al_2O_3 varies in most cases between 0.5 and 10%.

10 In accordance with another preferred embodiment of the invention, the suspension is subjected to a crushing operation. The crushing operation makes it possible to reduce the median diameter of the particles of the silico-aluminate.

The crushing operation is carried out in such a way as to produce for example a silico-aluminate which has a median particle diameter of between 0.5 and 20 μm , more particularly between 1 and 10 μm .

- 15 It has been found that the crushing operation makes it possible to increase the stability of the suspension in respect of time.

20 It will be noted that generally speaking, when the suspension is subjected to a crushing operation, the biogum is added after the crushing operation has been carried out. However, the addition of biogum to the suspension prior to the crushing operation is not excluded.

25 The suspensions of the invention may be used to advantage in the paper-making industry in the production of paper or cardboard in particular as a filler either in the body of or for coating of the paper or the cardboard. It will be appreciated that they are likewise suitable for all the usual uses of that type of substance, for example for polishing compositions, binding agents for catalytic compositions, additives for paints and for concrete and building and plastics materials.

Examples will now be set forth.

EXAMPLE 1

A filter cake of sodium silico-aluminate of the following composition is taken directly from the filter in the production process:

80.0% of SiO_2 - 9.35% of Al_2O_3 - 5.75% of Na_2O ,

- 5 which in the finished state after drying has a BET surface area of 100 m^2/g and a DOP absorption level of 170 ml/100 g. The firing loss of the cake is 74.3%.

The cake is slaked so as to produce a fluid pumpable slurry with a pH-value of 9.5.

- 10 That slurry is processed in a laboratory DYNO crusher provided with a 0.6 l glass bowl cooled by a double jacket and containing 450 cm^3 of glass balls of a diameter of 1.5 mm. The rate of crushing is 2000rpm and the flow rate at the outlet of the crusher is 250 cm^3/min .

- 15 Introduced by means of a four-blade turbine into the highly fluid crushed suspension which is produced in that way (median diameter of the particles is 2.2 μm), is xanthane gum of the type Rhodopol 50 MC which is marketed by RHONE-POULENC, in the following proportions:

- 450 g of crushed slurry (115 g of dry matter), and
- 1.15 g of Rhodopol 50 MC.

- 20 The mixture is agitated for 40 minutes at 600 rpm.

No deposit is observed after a period of 10 days. After a period of 40 days, a sedimentary volume (solid volume/total volume) of less than 1% is observed.

- 25 The fluidity of the product is good and its viscosity remains stable in respect of time.

COMPARATIVE EXAMPLE 2

The slurry which is prepared and crushed as in Example 1 is left at rest without the addition of xanthane gum.

Total sedimentation is observed after a period of 4 days. It is impossible to put it back into suspension.

EXAMPLE 3

The starting point for this Example is the slaked cake of Example 1 but it is not crushed. The median diameter of the particles is 11 μm .

0.25 g of RHODOPOL 50 MC is added to 450 g of slurry (115 g of dry matter), and agitation is effected as in Example 1.

No deposit is observed after a period of 10 days. After 40 days, a sedimentary volume of the order of 5% is observed.

10 EXAMPLE 4

The starting point for this Example is the slaked cake of Example 1. Added to 3500 g of that cake are 136 cm³ of 1.5 N H_2SO_4 and 569 g of dry silico-aluminate in powder form. The solids content of the suspension is then 34% and the pH-value is 8.9.

15 A crushing operation is effected, producing a highly fluid suspension (median particle diameter 2.3 μm).

2g of RHODOPOL 50 MC is added to that suspension and the mixture is agitated as in Example 1.

20 The mixture obtained, by virtue of its concentration, is in the form of a gel of low viscosity (after 17 days the viscosity is 57 mPa.s) which can be easily fluidified by applying a low level of stress energy (1 minute at 500 rpm).

EXAMPLE 5

25 The starting point for this Example is a dry sodium silico-aluminate of the formula: Na_2O , Al_2O_3 , 14 SiO_2 , $3\text{H}_2\text{O}$, with a pH-value of 10, a firing loss at 900°C of 12%, a DOP absorption level of 170 ml/100 g, a BET surface area of 100 m²/g and a compacted density of 0.3.

3 g of RHODOPOL 50 MC is added to 2500g of a suspension of 575 g of the above-indicated dry product in water. Agitation is effected for 1 hour. The final pH-value is 9.7.

After a period of 7 days, the suspension is still fluid. After
5 10 days, a sedimentary volume of 15% is observed. The suspension can be easily fluidified by applying a low level of stress energy (1 minute at 500 rpm).

It will be appreciated that the invention is in no way limited to the embodiments described which have been set forth only by way of
10 example. In particular it comprises all means constituting technical equivalents for the means described as well as combinations thereof if they are used within the scope of protection as claimed.



Translation of the German-language claims:

CLAIMS

1. A stable aqueous suspension characterised in that it comprises a synthetic amorphous silico-aluminate and, as a stabilising agent, a biogum.

2. A suspension according to claim 1 characterised in that it comprises an alkali metal silico-aluminate, in particular of sodium.

3. A suspension according to claim 2 characterised in that it comprises an amorphous silico-aluminate of the following formula:

$x \text{ Na}_2\text{O}, \text{Al}_2\text{O}_3, y \text{ SiO}_2, w \text{ H}_2\text{O}$ in which

$x = 0.1 \text{ to } 2; y = 1.5 \text{ to } 16; w = 0.3 \text{ to } 4.$

4. A suspension according to one of claims 1 to 3 characterised in that it comprises a silico-aluminate which is produced by precipitation and formed by a filter cake which results from the precipitation reaction and is slaked.

5. A suspension according to one of the preceding claims characterised in that it comprises a biogum which was produced by fermentation of carbohydrate by bacteria or fungi belonging to the genera Xanthomonas, Arthrobacter, Azotobacter, Agrobacter, Alcaligenes, Erwinia, Rhizobium, Corticium, Sclerotinia, Stromatinia or Sclerotium.

6. A suspension according to claim 5 characterised in that it comprises a xanthane gum.

7. A suspension according to one of the preceding claims characterised in that it has been subjected to a crushing operation.

8. Use of the suspensions according to one of the preceding claims in the production of papers and cardboards.