USE OF POLYASPARTIC ACID SALTS AS A GRINDING AID

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Claim

1. A grinding aid for obtaining aqueous suspensions of refined mineral substances which can be pumped, do not lend themselves to sedimentation and are highly concentrated in mineral substances, characterised in that said grinding aid is a salt of polyaspartic acids.
I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

[70,71] Applicant(s)/Nominated Person(s):
Coatex S.A., of 35, rue Ampere, Z.I. Lyon-Nord, 69730 Genay, FRANCE

[54] Invention Title:
Use of Polyaspartic Acid Salts as a Grinding Aid

[72] Inventor(s):
Jean-Marc Suau, Christian Jacquemet, Jacques Mongoin

[74] Address for service in Australia:
Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia (Code SF)

[31] Appl'n No(s):
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[33] Country:
FR

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Coatex S.A.

By:

Registered Patent Attorney

IRN: 407709

INSTR CODE: 52855
Australia
Patents Act 1990
Notice Of Entitlement

I, Eric Hessant, of 35, rue Ampere, Z.I. Lyon-Nord, 69730 Genay, FRANCE, being authorised by
the Applicant/Nominated Person in respect of an invention entitled:

Use of Polyaspartic Acid Salts as a Grinding Aid

state the following:-

The Applicant/Nominated Person has entitlement from the actual inventors as follows:

The Applicant/Nominated Person is the assignee of the actual inventors.

The Applicant/Nominated Person is the applicant of the basic application listed on the Patent
Request.

The basic application listed on the Patent Request is the first application made in a Convention
country in respect of the invention.

Dated March 2nd, 1998

[Signature]

Eric Hessant

IRN: 407709
Instructor Code: 052855
Name and Address of Applicant: Coatex S.A.
35, rue Ampere
Z.I. Lyon-Nord
69730 Genay
FRANCE

Actual Inventor(s): Jean-Marc Suau, Christian Jacquemet, Jacques Mongoin

Address for Service: Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Invention Title: Use of Polyaspartic Acid Salts as a Grinding Aid

The following statement is a full description of this invention, including the best method of performing it known to me/us:-
USE OF POLYASPARTIC ACID SALTS AS A GRINDING AID

The present invention relates to the use of polyaspartic acid salts as a grinding aid for grinding minerals in aqueous suspension.

The present invention also relates to the grinding method using polyaspartic acid salts as a grinding aid for grinding mineral substances in aqueous suspension.

Finally, the present invention relates to the aqueous suspensions of refined minerals containing said grinding aid and intended for pigment applications in the paper industry.

To make them fit for use in the field of pigments, the skilled person must convert these aqueous mineral suspensions by means of grinding into a very fine aqueous suspension, the constituent grains of which must be as small as possible, i.e. of a dimension less than a few micrometres.

At the same time, these suspensions must exhibit a Brookfield viscosity of a value at which there will be no risk of sedimentation or hard settling of particles of mineral substances, so as to ensure easy handling by the user even after several days of storage in tanks without agitation. Furthermore, these suspensions must have as high a mineral content as possible in order to keep down the production and transport costs inherent in the quantity of water present.

However, producing ideal suspensions incorporating these fundamental qualities faces the skilled person
with certain problems when it comes to using grinding methods on aqueous media, i.e. processes that will reduce the size of the particles of mineral substances and increase their specific surface area.

It should be noted that these problems, which might include a rapid increase in viscosity for example, due to the extreme fineness of the particles and encountered both during grinding operations using an aqueous medium and where the concentration of mineral is high, can lead to a build-up of suspensions in storage tanks or to the grinders becoming clogged but are not encountered during the suspending operations, the purpose of which is to place the mineral substances in suspension in water without changing the size of the particles making up said substances.

It has been known for a long time that water-soluble polymers with a base of polyacrylic acid or one of its derivatives can be used as a grinding agent (EP 0 100 947, EP 0 542 643, EP 0 542 644) in order to produce aqueous mineral suspensions which meet the above-mentioned quality criteria.

However, these various types of grinding agents known to the skilled person have a disadvantage in that they are not readily bio-degradable.

Until today, the profession has not come up with any satisfactory solutions to resolving this problem of finding a grinding aid for grinding mineral substances that will produce aqueous suspensions of refined mineral substances, highly concentrated in minerals, which do not lend themselves to sedimentation, can be pumped and meet current concerns relating to
environmental protection.

After a considerable amount of research, the applicant has now found that salts of polyaspartic acids can be used as a grinding aid as a means of overcoming the above-mentioned problems, namely as a means of obtaining aqueous suspensions of refined minerals which do not lend themselves to sedimentation, which can be pumped and are highly concentrated in mineral substances whilst at the same time using bio-degradable grinding agents. The use of such types of agent therefore opens up a way of using natural products which is completely new and different from the commonly known method of using acrylics.

Documents (WO 94/19409, WO 92/15535) disclose the use of polyaspartic acid salts as an agent for dispersing fillers such as calcium carbonate. However, there is no indication of such polymers being used as a grinding aid for grinding mineral substances in aqueous suspension, which can be pumped, do not lend themselves to sedimentation, are highly concentrated in dry substances and are intended for use in the paper industry.

No longer being able to rely on the knowledge of selecting acrylics by molecular weight, the latter being unrelated to those of aspartics, the applicant has now discovered that the use of certain salts of polyaspartic acids having a weight average molecular weight within a weight range between 3500 and 25000, preferably between 4000 and 10000, and more preferably between 5300 and 8000, will produce aqueous suspensions of refined mineral substances which can be pumped, which are highly concentrated in dry substances and
which do not lend themselves to sedimentation.

Consequently, one of the objectives of the invention is to use polyaspartic acid salts as a grinding aid in order to produce aqueous suspensions of mineral substances with a capacity to be pumped, which do not sediment, are highly concentrated in mineral substances and are refined, i.e. mineral substances which can be pumped, do not sediment, are highly concentrated in mineral substance, the constituent grains of which are of the finest size possible, namely a mean diameter of less than three micrometres, preferably less than one micrometre, and whose Brookfield viscosity increases only slightly over time, i.e. up to a value that will still make for easy manipulation by the user even if stored for several days or even several weeks in tanks without any agitation.

Another objective of the invention is to provide a method of grinding mineral particles in aqueous suspension using selected salts of polyaspartic acids as a grinding aid.

A further objective of the invention is to provide aqueous suspensions of refined mineral substances which do not sediment, can be pumped and are highly concentrated in mineral substances.

For the purposes of the invention, these suspensions, intended for use in pigment applications and the constituent grains of which are of the finest possible dimensions, i.e. have a mean diameter of less than three micrometres and preferably less than one micrometre, have a Brookfield viscosity which increases only slightly over time and are highly concentrated in
mineral substances, i.e. contain at least 70% mineral substances.

Another objective of the invention relates to the use of these aqueous suspensions of refined minerals as a bulk filler and for coating paper.

These objectives are achieved by using salts of polyaspartic acids of the invention as a grinding aid.

In particular, these polyaspartic acid salts are produced by hydrolysis and by neutralising the products obtained by a process of thermally condensing the aspartic acids with or without a catalyst, such as a strong acid, for example, which will increase the molecular weight, or alternatively a hydroxylated polycarboxylic acid in order to decrease the molecular weight. These salts may also be produced by processing and fractionating polyaspartic acid salts, statically or dynamically using one or more solvents, these polyaspartic acid salts being synthesised by a process of thermal condensation of the aspartic acids, in turn produced by any method of synthesis known to the person skilled in the art, such as enzymatic synthesis based on starch, for example, or alternatively by chemical means using maleic anhydride and/or fumaric acid. These salts of polyaspartic acids are selected from among the polyaspartic acid salts having a weight average molecular weight, measured by GPC in aqueous phase graded using standard sodium polyacrylates marketed by the company, Polymer Standards Services (Germany), in a weight range between 3500 and 25000, preferably between 4000 and 10000, more preferably between 5300 and 8000, and are also selected from among the polyaspartates neutralised by at least one hydrolysing and
neutralising agent having a monovalent function or by combining at least one hydrolysing and neutralising agent having a monovalent agent with at least one hydrolysing and neutralising agent having a polyvalent function.

In order to provide a more comprehensive understanding of the objectives of the invention, it should be noted that by hydrolysing and neutralising agent having a monovalent function, the applicant means agents which have the capacity to react with the imide site which is the precursor to the polyaspartic acid and that by hydrolysing and neutralising agent having a polyvalent function, the applicant means agents having the capacity to react with the number of imide sites which are precursors to the polyaspartic acid and correspond to the valence of the neutralising cation.

Similarly, by polyaspartic acids the applicant means the homopolymers of aspartic acids resulting from thermal polycondensation, catalysed or not, of aspartic acids (L-aspartic acid or D-aspartic acid or mixtures thereof) or resulting from the use of maleic anhydride and/or fumaric acid. By polyaspartic acids is also meant mixtures of homopolymers of aspartic acids with homopolymers of acrylic acid or with polysuccinimide or, finally, mixtures of homopolymers of aspartic acids with copolymers of acrylic acid with other ethylenically unsaturated monomers such as methacrylic acid, maleic anhydride, acrylamide, methacrylamide, acrylamido-methyl-propane-sulphonic acid, hydroxy ethyl and/or methyl phosphoric ester of acrylate and/or methacrylate or mixtures thereof, for example.

The hydrolysing and neutralising agent with a
monovalent function is chosen for example from the group comprising the compounds containing the alkaline cations, in particular sodium and potassium, or alternatively ammonium, or else the aliphatic and/or cyclic primary or secondary amines such as the ethanolamines, mono- and diethylamine or cyclohexylamine, for example.

The hydrolysing and neutralising agent with a polyvalent function is in turn selected from among the groups comprising the compounds containing alkaline earth divalent cations, in particular magnesium and calcium, or alternatively zinc, as well as the trivalent cations, of which aluminium in particular, or else by certain compounds containing cations of a higher valency.

The hydrolysis and neutralisation reaction of the polyaspartic acid precursor imide sites can be produced by possible combinations between at least one hydrolysing and neutralising agent having a monovalent function and at least one hydrolysing and neutralising agent having a polyvalent function.

Of the pairs or trios of hydrolysing and neutralising agents, it is common practice to use pairs or trios consisting of an agent having a monovalent function and an agent having a divalent or trivalent function, such as the pairs or trios (Na⁺ and/or K⁺ and/or NH₄⁺ and Ca²⁺), (Na⁺ and/or K⁺ and/or NH₄⁺ and Mg²⁺), (Na⁺ and/or K⁺ and/or NH₄⁺ and Zn²⁺), (Na⁺ and/or K⁺ and/or NH₄⁺ and Al³⁺), (Na⁺ and/or K⁺ and/or NH₄⁺ and amine).

All these hydrolysis and neutralisation combinations can be restricted to a few examples to illustrate the
potential of the invention.

Each hydrolysing and neutralising agent giving rise to the polymer used as a grinding aid for the purposes of the invention will occur at the neutralisation rates specific to each valency function.

In one embodiment, the polyaspartic acid salts, intended for use in accordance with the invention as a grinding aid, may be the fraction of these salts produced by known methods of synthesising polyaspartic acids which are then separated to obtain polyaspartic acid salts whose weight average molecular weight is between 3500 and 25000, preferably between 4000 and 10000 and more preferably between 5300 and 8000 measured by GPC in aqueous phase, graded by means of standard sodium polyacrylates marketed by the Polymer Standards Service (Germany) under the names PSS-PAA varying from 18000 to 2000 grams/mole (Mw). At this stage, it should be pointed out that all the weight average molecular weights of the polyaspartic acid salts indicated throughout the present application are determined by GPC in aqueous phase graded by means of standard sodium polyacrylates marketed by the Polymer Standards Service (Germany) under the names of PSS-PAA varying within the weight range from 18000 to 2000 grams/mole (Mw).

Consequently, the fraction of the salt of polyaspartic acids having a weight average molecular weight in the weight range between 3500 and 25000, preferably between 4000 and 10000 and more preferably between 5300 and 8000 intended for use as a grinding aid, is generally isolated and extracted from the solution produced by hydrolysis and neutralisation of polyaspartic acids.
with at least one hydrolysing and neutralising agent having a monovalent function or by combining at least one hydrolysing and neutralising agent having a monovalent function with at least one hydrolysing and neutralising agent having a polyvalent function, whether these polyaspartic acids be a homopolymer of aspartic acids such as L-aspartic acid or D-aspartic acid or mixtures thereof or alternatively a mixture of homopolymers of aspartic acids with polysuccinimide or with homopolymers or copolymers of acrylic acid.

This polymer solution resulting from the hydrolysis and neutralisation process is treated by static or dynamic methods known to the person skilled in the art using one or more polar solvents belonging in particular to the group comprising water, methanol, ethanol, propanol, isopropanol, the butanols, acetone, tetrahydrofurane or mixtures thereof. A separation into two phases is then produced and these are recovered, at least one of them being the fraction of the salts of polyaspartic acid hydrolysed and neutralised by at least one hydrolysing and neutralising agent having a monovalent function or by the combination of at least one hydrolysing and neutralising agent having a monovalent function with at least one hydrolysing and neutralising agent having a polyvalent function. This fraction has a weight average molecular weight in the weight range between 3500 and 25000, preferably between 4000 and 10000 and more preferably between 5300 and 8000.

The phases obtained may then be put through a process of distillation in order to remove the solvent or solvents used for the purposes of fractionation. Under certain conditions, it is also possible and desirable
to fine down still further the selection of the fraction of polyaspartic acid salts by re-treating the phases previously recovered using a fresh quantity of polar solvent, which may be different from the one originally used or which may alternatively be a mixture of polar solvents. Once again, two phases will appear, at least one of which is recoverable which will be the fraction of polyaspartic acid salts whose weight average molecular weight falls within a narrower weight range. In practice, it is of interest to select the fraction of polyaspartic acid salts hydrolysed and neutralised by at least one hydrolysing and neutralising agent having a monovalent function or by combining at least one hydrolysing and neutralising agent having a monovalent function with at least one hydrolysing and neutralising agent having a polyvalent function and whose weight average molecular weight is within the weight range between 3500 and 25000, preferably between 4000 and 10000 and more preferably between 5300 and 8000.

The resulting liquid phase containing polyaspartic acid salts can be used in this form as a grinding aid for grinding the mineral substances to be refined but it may also be treated by any known method in order to remove and isolate the polyaspartic acids from this phase in the form of a fine powder which can then be used in this other form as a grinding aid.

In practical terms for the purposes of the invention, the operation whereby the mineral substance is ground consists in refining said substances into very fine particles using a grinding medium in an aqueous medium containing the salt of polyaspartic acids used as a grinding aid. This latter is used to form an aqueous
suspension of the mineral substance to be ground, the particles of which are of an initial dimension of not more than 50 micrometres, and is used in a quantity such that the concentration of dry substance in said suspension is at least 70% by weight.

The grinding medium, whose grain size is advantageously within a range of between 0.2 millimetres and 4 millimetres is added to the suspension of the substance to be ground. The grinding medium is generally in the form of particles of substances which may be as diverse as silicon oxide, aluminium oxide, zirconium oxide or mixtures thereof as well as the high hardness synthetic resins, steels or others.

The grinding medium is preferably added to the suspension in such a quantity that the ratio by weight of this grinding substance to the mineral substance to be ground is at least 2/1, this ratio preferably falling within the limits of 3/1 and 5/1.

The mixture of the suspension and grinding medium is then put through a mechanical grinding process, such as that produced in a conventional grinder with micro-elements.

The grinding aid is also introduced into the mixture formed by the aqueous suspension of mineral substances and the grinding medium in a quantity of 0.2 to 2% by weight of dried fraction of said polymers relative to the dry mass of the mineral substance to be ground.

The time required to obtain a perfectly fine mineral substance after grinding will vary depending on the nature and quantity of the mineral substances to be
refined and depending on the agitation mode used and the ambient temperature during the grinding operation.

The grinding method of the invention based on an aqueous suspension which is highly concentrated in mineral substances for use in pigment applications and consisting in refining these mineral particles into very fine particles in an aqueous suspension is, therefore, characterised in that a grinding aid is used, comprising salts of polyaspartic acids having a weight average molecular weight in a weight range between 3500 and 25000, preferably between 4000 and 10000 and more preferably between 5300 and 8000, in a quantity of 0.2% to 2% by dry weight relative to the dry weight of mineral substances.

The grinding method of the invention is also characterised in that the aqueous suspension of mineral substances to be ground contains at least 70% by weight of dry substance.

The mineral substances to be ground by the method of the invention may be of very varied origins such as natural or synthetic calcium carbonate, the dolomites, i.e. all the mineral substances which have to be ground before they can be used in applications such as those inherent in paper manufacture or paper coating.

The use of polyaspartic acid salts as grinding aid in accordance with the invention as a means of producing aqueous suspensions of refined mineral substances by grinding, i.e. of a mean diameter of less than three micrometres and preferably less than one micrometre, which can be pumped, which do not sediment and are highly concentrated in mineral substances, is
characterised in that said salt of polyaspartic acids is a salt of polyaspartic acids hydrolysed and neutralised by at least one hydrolysing and neutralising agent having a monovalent function or by the combination of at least one hydrolysing and neutralising agent having a monovalent function with at least one hydrolysing and neutralising agent having a polyvalent function and in that it has a weight average molecular weight in a weight range between 3500 and 25000, preferably between 4000 and 10000 and more preferably between 5300 and 8000.

The aqueous suspensions of the invention obtained by using salts of aspartic acids as grinding aid are characterised in that they contain a polyaspartic acid salt in a quantity of 0.2 to 2% by dry weight relative to the dry weight of mineral substances and in that the mean diameter of the refined particles is less than three micrometres, preferably less than one micrometre, and the concentration of dry mineral substances is at least 70%.

The grain size of the mineral particles is determined using the Sedigraph 5100 x-ray granulometer marketed by Micromeritics.

The scope and interest of the invention will be more readily understood from the following examples, which are not restrictive in any respect.

**EXAMPLE 1**

The purpose of this example is to illustrate the use of various polyaspartic acid salts as a grinding aid.
To this end, for each of the tests in the example, an aqueous suspension was prepared to a 76% concentration by weight of coarse calcium carbonate using a natural calcium carbonate from the Orgon deposit (France), the particle sizes of which are at most 50 micrometres, and using:

- for test N°1 illustrating the invention, a polyaspartate neutralised 100% mole by soda and having a weight average molecular weight expressed as $M_w = 10 \, 5700$,

- for test N°2 illustrating the invention, a polyaspartate neutralised 90% mole by soda and 10% mole by lime and having the same weight average molecular weight as that of the preceding test,

- for test N°3 illustrating the invention, a polyaspartate neutralised 80% mole by soda and 20% mole by lime and having the same weight average molecular weight as that of test N°1,

- for test N°4 illustrating the invention, a polyaspartate neutralised 75% mole by soda and 25% mole by lime and having the same weight average molecular weight as that of the preceding test,

- for test N°5 illustrating the invention, a polyaspartate neutralised 70% mole by soda and 30% mole by lime and having the same weight average molecular weight as that of test N°1,

- for test N°6 illustrating the invention, a polyaspartate neutralised 70% mole by soda and 30% mole by magnesium hydroxide and having the same weight
average molecular weight as that of test N°1,

- for test N°7 illustrating the invention, a polyaspartate neutralised 65% mole by soda and 35% mole by lime and having the same weight average molecular weight as that of test N°1,

- for test N°8 illustrating the invention, a polyaspartate neutralised 60% mole by soda and 40% mole by magnesium hydroxide and having the same weight average molecular weight as that of test N°1,

- for test N°9 illustrating the invention, a polyaspartate neutralised 55% mole by soda and 45% mole by magnesium hydroxide and having the same weight average molecular weight as that of test N°1,

- for test N°10 illustrating the invention, a polyaspartate neutralised 50% mole by soda and 50% mole by magnesium hydroxide and having the same weight average molecular weight as that of test N°1,

- for test N°11 illustrating the invention, a polyaspartate neutralised 45% mole by soda and 55% mole by magnesium hydroxide and having the same weight average molecular weight as that of test N°1.

For each of the tests, the grinding aid is introduced into this suspension in accordance with the quantities indicated in the table below, expressed as a percentage dry weight relative to the mass of dry calcium carbonate to be ground.

The suspension circulates in a grinder of the Dyno-Mill type with a fixed cylinder and rotating impeller, the
grinding medium consisting of corundum beads of a
diameter ranging between 0.6 millimetre and 1.0
millimetre.

The total volume occupied by the grinding medium is 1
5 150 cubic centimetres and its weight is 2 900 g.

The volume of the grinding chamber is 1 400 cubic
centimetres.

The circumferential speed of the grinder is 10 metres
per second.

The calcium carbonate suspension is recycled at a rate
of 18 litres per hour.

The output of the Dyno-Mill grinder is fitted with a
separator with a mesh size of 200 microns so that the
suspension produced by the grinding process can be
separated from the grinding medium. The temperature is
maintained at approximately 60°C for each of the
grinding tests.

At the end of the grinding process (T0), a sample of
the pigment suspension is collected in a flask, 80% of
the particles of which are less than one micrometre in
size, and the viscosity is measured using a Brookfield
viscometer of the RVT type, at a temperature of 20°C and
rotation speeds of 10 revolutions per minute and 100
revolutions per minute with the appropriate spindle.

After a resting time of 8 days in the flask, the
viscosity of the suspension is measured by introducing
into the flask, without agitation, the appropriate
spindle of the RVT Brookfield viscometer at a temperature of 20°C and at rotation speeds of 10 revolutions per minute and 100 revolutions per minute (viscosity AVAG = before agitation).

Similarly, after a short and vigorous agitation, the viscosity of the suspension is measured again at a temperature of 20°C and rotation speeds of 10 revolutions per minute and 100 revolutions per minute (viscosity APAG = after agitation).

All the experimental results are set out in table 1 below and it should be pointed out that none of the tests exhibited any sedimentation of calcium carbonate.

In fact, a visual inspection of each of the resting flasks did not reveal any supernatant on the surface of the samples nor did the introduction of a spatula into each of the flasks reveal any hard deposit on the base of said flasks.
<table>
<thead>
<tr>
<th>Test N°</th>
<th>GRINDING AID USED</th>
<th>Brookfield viscosity of the suspension (at 20°C in mPa.s) with 76% dry substance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Neutralisation Rate-ion Rate-ion (%)</td>
<td>Mw</td>
</tr>
<tr>
<td>Invention 1</td>
<td>100 Na</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 2</td>
<td>90 Na/10 Ca</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 3</td>
<td>80 Na/20 Ca</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 4</td>
<td>75 Na/25 Ca</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 5</td>
<td>70 Na/30 Ca</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 6</td>
<td>70 Na/30 Mg</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 7</td>
<td>65 Na/35 Ca</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 8</td>
<td>60 Na/40 Mg</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 9</td>
<td>55 Na/45 Mg</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 10</td>
<td>50 Na/50 Mg</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 11</td>
<td>45 Na/55 Mg</td>
<td>5700</td>
</tr>
</tbody>
</table>

AVAG : Viscosity measurement before agitating the suspension  
APAG : Viscosity measurement after agitating the suspension
Table 1 demonstrates that it is possible to produce aqueous suspensions of refined calcium carbonate, with a high concentration of calcium carbonate which does not sediment and can be pumped, i.e. can be manipulated by the user.

EXAMPLE 2:

The purpose of this example is to illustrate the use of polyaspartic acid salts of differing molecular weights.

To this end, an aqueous suspension of natural calcium carbonate from the Orgon deposit (France), the particles of which are of a dimension of at most 50 micrometres, is ground for each of the tests under the same operating conditions and using the same equipment as in the preceding example, using polyaspartic acid salts of different molecular weights.

Test N°12:
This test illustrates the use of a polyaspartate neutralised 50% mole by soda and 50% mole by magnesium hydroxide, of a weight average molecular weight expressed as $M_w = 1200$.

This salt of polyaspartic acids was obtained by using isopropanol to fractionate a salt of polyaspartic acids neutralised 50% mole by soda and 50% mole by magnesium hydroxide and having a weight average molecular weight expressed $M_w = 5700$.

The applicant was unable to grind the calcium carbonate suspension with a 76% concentration due to a rapid and consequent increase in the Brookfield viscosity in spite of adding an extra quantity of more than 2% by
I dry weight of said polyaspartate relative to the total weight of mineral substances.

**Test No. 13:**
This test illustrates the use of a polyaspartate neutralised 50% mole by soda and 50% mole by magnesium hydroxide, of a weight average molecular weight expressed as $M_w = 1800$.

As above, this salt of polyaspartic acids was obtained by using isopropanol to fractionate a salt of polyaspartic acids neutralised 50% mole by soda and 50% mole by magnesium hydroxide and having a weight average molecular weight expressed $M_w = 5700$.

As was previously the case, the applicant was not able to grind the calcium carbonate suspension concentrated to 76% because of the rapid and consequent increase in the Brookfield viscosity of the suspension.

**Test No. 14:**
This test illustrates the use of a polyaspartate neutralised 70% mole by soda and 30% mole by lime, having a weight average molecular weight expressed $M_w = 2400$ obtained by using isopropanol to fractionate a salt of polyaspartic acids neutralised 70% mole by soda and 30% mole by lime and of a weight average molecular weight expressed $M_w = 5700$.

For the same reasons as those outlined in tests No. 12 and 13, grinding was again impossible at a 76% concentration.

**Test No. 15:**
This test illustrates the use of a salt of polyaspartic
acids with a weight average molecular weight expressed as $M_w = 3700$.

To this end, an aqueous suspension of coarse calcium carbonate with a 76% concentration of dry substance was prepared from the same natural calcium carbonate as that used in the preceding tests using the same equipment and the same operating mode as described above.

Grinding could not be continued beyond a fineness corresponding to 66% of particles having a diameter of less than one micrometre because of a too high increase in the Brookfield viscosity in spite of adding an extra 1.23% by dry weight of grinding aid relative to the dry weight of calcium carbonate to be refined.

Test N°16:
This test illustrates the use of a polyaspartate neutralised 50% mole by soda and 50% mole by magnesium hydroxide, having a weight average molecular weight expressed as $M_w = 4200$ obtained by fractionating with isopropanol a polyaspartate neutralised 50% mole by soda and 50% mole by magnesium hydroxide and having a weight average molecular weight expressed by $M_w = 5700$.

It was possible to grind with an 80% grain size distribution of particles having a diameter of less than one micrometre using the same equipment and the same operating conditions as those of the preceding tests.

Test N°17:
This test illustrates the invention using the polyaspartate of test N°10.
Test N°18:
This test illustrates the use of a polyaspartate neutralised 50% mole by soda and 50% mole by magnesium hydroxide, having a weight average molecular weight expressed as $M_w = 7350$ obtained by fractionating with isopropanol a polyaspartate neutralised 50% mole by soda and 50% mole by magnesium hydroxide and having a weight average molecular weight expressed as $M_w = 5700$.

It was possible to grind at 80% grain size distribution of particles having a diameter of less than one micrometre using the same equipment and the same operating conditions as those of the preceding tests.

Test N°19:
This test illustrates the use of a sodium polyaspartate having a weight average molecular weight expressed as $M_w = 21600$.

The salt of polyaspartic acids was obtained by putting aspartic acids through a process of thermal condensation in the presence of phosphoric acid followed by hydrolysis of the entire imide function by soda and magnesium hydroxide.

To this end, an aqueous suspension of coarse calcium carbonate comprising a 76% concentration of dry substance was prepared from the same natural calcium carbonate as that used for the preceding tests using the same equipment and the same operating mode as described above.

Grinding could not be continued beyond a fineness corresponding to 60% of the particles with a diameter
of less than one micrometre because there was too high an increase in the Brookfield viscosity in spite of the fact that an extra 1.37% by dry weight of grinding aid was added relative to the dry weight of calcium carbonate to be refined.

The results of the various grinding test using the different quantities of grinding aid used in the example are set out in table 2 below, and it should be pointed out that, as with the previous example, no sedimentation was observe...
### TABLE 2

<table>
<thead>
<tr>
<th>Test N°</th>
<th>GRINDING AID USED</th>
<th>Brookfield viscosity of the suspension (at 20°C in mPa.s) with 76% dry substance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Neutralisation Rate-Ion/Rate-Ion (%)</td>
</tr>
<tr>
<td>12</td>
<td>50 Na/50 Mg</td>
<td>1200</td>
</tr>
<tr>
<td>13</td>
<td>50 Na/50 Mg</td>
<td>1800</td>
</tr>
<tr>
<td>14</td>
<td>70 Na/30 Ca</td>
<td>2400</td>
</tr>
<tr>
<td>Invention 15</td>
<td>100 Na</td>
<td>3700</td>
</tr>
<tr>
<td>Invention 16</td>
<td>50 Na/50 Mg</td>
<td>4200</td>
</tr>
<tr>
<td>Invention 17</td>
<td>50 Na/50 Mg</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 18</td>
<td>50 Na/50 Mg</td>
<td>7350</td>
</tr>
<tr>
<td>Invention 19</td>
<td>50 Na/50 Mg</td>
<td>21600</td>
</tr>
</tbody>
</table>

1.23* Corresponds to the quantity of agent used for a grain size of 66% < 1 μm. Grinding was impossible beyond 66% < 1 μm.
1.37** Corresponds to the quantity of agent used for a grain size of 60% < 1 μm. Grinding was impossible beyond 60% < 1 μm.

**AVAG**: Viscosity measurement before agitating the suspension
**APAG**: Viscosity measurement after agitating the suspension
It is clear from table 2 that highly concentrated (76%) calcium carbonate can be ground in aqueous suspension using aspartic acid salts having a weight average molecular weight in a weight range between 3500 and 25000, more especially between 4000 and 10000 and most especially between 5300 and 8000.

In effect, the results obtained for tests N°15 and 19 highlight the fact that the use of grinding aid with a weight average molecular weight expressed as Mw 3700 or 21600 allows concentrated aqueous suspensions of calcium carbonate to be obtained, which can be pumped, does not form sediment and are fine enough to be used in applications such as a filler for paper without obtaining the extremely fine suspensions such as those of tests N°16 and 18 which can be used in applications such as coating paper.

Table 2 also highlights marked differences in Brookfield viscosity after 8 days of storage and before agitation in respect of the suspension of test N°16 (in which an agent with a weight average molecular weight expressed as Mw = 4200 was used) and those of the suspensions of tests N°17 and 18 (using agents of weight average molecular weight expressed as Mw = 5700 and Mw = 7350).

EXAMPLE 3:
The purpose of this example is to illustrate the use of mixtures of polyaspartic acid salts with acrylic homopolymers or copolymers or with polysuccinimide as grinding aid.

To this end, for each of the tests in this example, an aqueous suspension of natural calcium carbonate from
the Orgon deposit (France) having an average diameter of 50 micrometres is ground under the same operating conditions and with the same apparatus as in the preceding examples using:

5 Test N°20:
A mixture in a ratio of 75% by weight of a polyaspartate neutralised 50% mole by soda and 50% mole by magnesium hydroxide of $\text{Mw} = 5700$ with 25% by weight of a polyacrylate neutralised 50% mole by soda and 50% mole by magnesium hydroxide, of the same weight average molecular weight.

Test N°21:
A mixture of the same polymers in a ratio by weight of 50% polyaspartate - 50% polyacrylate.

15 Test N°22:
A mixture of the same polymers in a ratio by weight of 25% polyaspartate - 75% polyacrylate.

Test N°23:
A mixture in a ratio of 25% by weight of a polyaspartate neutralised 50% mole by soda and 50% mole by magnesium hydroxide of $\text{Mw} = 5700$ with 75% by weight of a copolymer of the same weight average molecular weight expressed as $\text{Mw} = 5700$ neutralised 50% mole by soda and 50% mole by magnesium hydroxide and consisting of 95% by weight of acrylic acid and 5% of acrylamide.

Test N°24:
A mixture in a ratio by weight of 83% of a polyaspartate neutralised 50% mole by soda and 50% mole by magnesium hydroxide of $\text{Mw} = 5700$ with 17% by weight of a polysuccinimide having the same weight average molecular weight.
molecular weight.

Grinding could not be continued beyond a fineness corresponding to 76% of the particles having a diameter of less than one micrometre because of a too high increase in the Brookfield viscosity in spite of the fact that an additional 1.35% by dry weight of grinding aid was added relative to the dry weight of calcium carbonate to be refined.

The results of the various grinding tests using the different quantities of grinding aid are set out in table 3 below: as was the case in the preceding examples, the various tests showed evidence of no sedimentation.
- TABLE 3 -

<table>
<thead>
<tr>
<th>Test N°</th>
<th>GRINDING AID USED</th>
<th>Brookfield viscosity of the suspension (at 20°C in mPa.s) with 76% dry substance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mixture Polyaspartate (Polyaspartate (Polyaspartate (Polyaspartate (%)</td>
<td>(%</td>
</tr>
<tr>
<td>Invention 20</td>
<td>75/25</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 21</td>
<td>50/50</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 22</td>
<td>25/75</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 23</td>
<td>25/75</td>
<td>5700</td>
</tr>
<tr>
<td>Invention 24</td>
<td>83/17 (Polysuccinimide)</td>
<td>5700</td>
</tr>
</tbody>
</table>

1.35* Corresponds to the quantity of agent used for a grain size of 76% < 1 μm. Grinding was impossible beyond 76% < 1 μm.

AVAG : Viscosity measurement before agitating the suspension
APAG : Viscosity measurement after agitating the suspension
It is evident from table 3 that aqueous suspensions of calcium carbonate can be ground using mixtures of polyaspartic acid salts with acrylic acid homopolymers or copolymers or with a polysuccinimide as grinding aid.
The claims defining the invention are as follows:

1. A grinding aid for obtaining aqueous suspensions of refined mineral substances which can be pumped, do not lend themselves to sedimentation and are highly concentrated in mineral substances, characterised in that said grinding aid is a salt of polyaspartic acids.

2. A grinding aid as claimed in claim 1, characterised in that said salt has a weight average molecular weight expressed as Mw ranging between 3500 and 25000 measured by aqueous GPC.

3. A grinding aid as claimed in one of claims 1 or 2, characterised in that the polyaspartic acid salt is hydrolysed and neutralised by at least one hydrolysing and neutralising agent having a monovalent function or by the combination of at least one hydrolysing and neutralising agent having a monovalent function with at least one neutralising agent having a polyvalent function.

4. A grinding aid as claimed in any one of claims 1 to 3, characterised in that the polyaspartic acid salt is a salt of a homopolymer of aspartic acids.

5. A grinding aid as claimed in any one of claims 1 to 3, characterised in that the polyaspartic acid salt is a mixture of homopolymer of aspartic acid salt with a polysuccinimide or a mixture of homopolymer of aspartic acid salt with an acrylic homopolymer or copolymer salt selected from acrylic, methacrylic, acrylamido-methyl-propane-sulphonic acid or from maleic anhydride, acrylamide, methacrylamide, phosphoric ester of hydroxy-ethyl and/or methyl acrylate and/or methacrylate and mixtures thereof.

6. A grinding aid as claimed in claim 3, characterised in that the hydrolysing and neutralising agent having a monovalent function belongs to the group comprising the compounds containing sodium, potassium, ammonium cations or alternatively primary or secondary amine.

7. A grinding aid as claimed in claim 3, characterised in that the hydrolysing and neutralising agent having a polyvalent function belongs to the group comprising the compounds containing the calcium, magnesium, zinc or aluminium cations.

8. A grinding aid as claimed in any one of claims 1 to 7, characterised in that said grinding aid has a weight average molecular weight in the Mw weight range between 4000 and 10000 measured by aqueous GPC.

9. A grinding aid as claimed in claim 8, characterised in that said grinding aid has a weight average molecular weight in the Mw weight range between 5300 and 8000 measured by aqueous GPC.

10. A grinding aid as claimed in any one of claims 1 to 9, characterised in that said grinding aid is a solution.

11. A grinding aid as claimed in any one of claims 1 to 9, characterised in that said grinding aid is a powder.

12. A grinding aid, substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples.
13. A method of grinding coarse mineral substances in aqueous suspension for use in pigment applications, consisting in preparing an aqueous suspension of these substances, introducing a grinding aid comprising polyaspartic acid salts, adding a grinding medium to the suspension and subjecting the mixture thus produced to a grinding action, characterised in that said grinding aid is as described in any one of claims 1 to 12.

14. A method of grinding mineral substances in aqueous suspension as claimed in claim 13, characterised in that the grinding aid is introduced into the suspension in a quantity of from 0.2% to 2% by dry weight of said polymer relative to the dry weight of the mineral substance to be ground.

15. A method of grinding mineral substances in aqueous suspension as claimed in any one of claims 13 or 14, characterised in that the aqueous suspension of mineral substances to be ground contains at least 70% by weight of dry substances.

16. A method of grinding coarse mineral substances in aqueous suspension, substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples.

17. An aqueous suspension of mineral substances ground using the grinding method as claimed in any one of claims 13 to 16, characterised in that it contains 0.2 to 2% by dry weight of a polyaspartic acid salt as described in any one of claims 1 to 12 relative to the dry weight of mineral substances, the concentration of mineral substances is at least 70%, and the median diameter, determined by measurement using the Sedigraph 5100, of refined particles is less than three micrometres.

18. An aqueous suspension of mineral substances as claimed in claim 17 characterised in that the median diameter of refined particles is less than one micrometre.

19. An aqueous suspension of mineral substances as claimed in claim 17 or claim 18 characterised in that the mineral substance is chosen from among natural calcium carbonate, synthetic calcium carbonate or the dolomites.

20. An aqueous suspension of mineral substances, substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples.

21. A paper filler containing the aqueous suspension of any one of claims 17 to 21.

22. A paper coating composition containing the aqueous suspension of any one of claims 17 to 21.

Dated 12 February, 1998
Coatex S.A.

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON
ABSTRACT

Use of polyaspartic acid salts as a grinding aid as a means of producing aqueous suspensions of refined mineral substances which can be pumped, do not lend themselves to sedimentation and are highly concentrated in mineral substances.

A grinding method using said grinding aid.

Aqueous suspensions of mineral substances obtained and their application in the paper industry.