

METHOD FOR PRODUCING PIGMENTARY PARTICLES THAT ARE
SELF-BINDING, DRY, OR IN AQUEOUS SUSPENSION OR DISPERSION,
AND CONTAIN INORGANIC MATERIALS AND BINDING AGENTS

- 5 The invention concerns a process for the manufacture of self-binding pigmentary particles, dry or in aqueous suspension or dispersion, containing at least one inorganic matter and at least one binder.

Inorganic particles and the polymer binders are two of the essential components used in
10 the manufacture of various coatings; the inorganic particles, generally calcium carbonate, contribute to the final product certain properties such as optical properties, and the binders, generally in the form of latex suspensions or dispersions, give an overall cohesion to all the constituent elements used in the process to manufacture coating compositions.

15

However, it has been known for many years that complex interactions may occur between the calcium carbonate and all the forms of binders, causing the final properties of the coating products to be modified. For example, "Physical and chemical modifications in latex binders and their effect on the coating colour rheology" (Advanced
20 Coating Fundamentals Symposium, San Diego, CA, United States, May 4-5, 2001, pp. 108-123) concerns the influence of the physical and chemical modifications in a dispersion of styrene-butadiene binders on the rheological properties of a wet pigmentary coating composition.

- 25 For a long time the production of self-binding pigmentary particles has been sought: solid particles containing a polymeric binder and an inorganic pigment which act as a single material, thus preventing the end user from losing specifications due to undesirable interactions in various applications.

It was initially advanced that such self-binding pigments differ from the well-known
30 pigmentary granulates through the nature of the forces assuring cohesion of these composite particles.

For example, document WO 01/00712 presents dry pigmentary granulates comprising 5 % to 99 % by weight of organic polymer pigment, from 0 % to 94.5 % by weight of

inorganic pigment and from 0.5 % to 5 % by weight of a binder or mixture of binders. Such granulates are manufactured by mixing all the constituents in dispersion and by drying by spraying of the said dispersion.

- 5 In addition, document WO 01/00713 describes plastic polymer pigments, applicable in a dry form, which can be hollow or solid, containing a polymer, a binder and an inorganic pigment.

As the inventors mention themselves, the conglomerates obtained consist of individual
10 spherical particles bound together by electrostatic forces.

According to a different viewpoint, the concept of self-binding pigments must be considered in this document as mutually bound individual particles, in which the binding mechanisms use not only electrostatic forces but also chemical bindings created through
15 sorption chemistry mechanisms, or physical bindings such as acid-base interactions between the inorganic matter and the polymeric binders and Lifshitz/van der Waals interactions.

In accordance with this concept, document WO 93/11183 describes a process to prepare
20 stable aqueous dispersions by forming two aqueous suspensions of inorganic matter and polymeric latex particles, by adjusting the Zeta potential of the suspensions, and finally by mixing the two suspensions. The Zeta potential may be modified through the use of an additive allowing the surface charge to be adjusted. The polymeric latex binder is supposed to be adsorbed strongly on the inorganic matter particles.

25

In addition, document WO 93/12183 teaches a process for the preparation of aqueous dispersions of composite particles comprising a latex and an inorganic matter, used in paints and coatings. The said polymeric latex particles act as a binder, contributing the necessary spacing between the inorganic particles to give the end product opacity and the
30 brightness. The process is characterised in that the latex prepared by polymerisation in emulsion is mixed in an aqueous suspension of inorganic matter, which suspension of inorganic matter is pre-dispersed with poly(meth)acrylic acid or its salts, or copolymer polyelectrolytes of (meth)acrylic acid or its salts. The authors suppose that the dispersant of the pigment does not cover the entire surface of the inorganic matter, and that at least

one portion of the said surface is available for the adsorption of the polymeric latex particles.

Finally, document US 4 025 483 describes a process to increase the stability of titanium
5 dioxide aqueous suspensions, by mixing the latter with polymeric latex particles. According to the examples, the polymeric latex particles increase the effectiveness of the dispersing agent which is contained in the initial inorganic matter suspension.

In the light of the prior art, the pigment-polymer particles can be obtained according to
10 various processes which always make reference to the use of a third constituent, such as a dispersing agent or an additive allowing the surface charge to be adjusted, to formulate the initial aqueous suspensions which contain the inorganic matter on the one hand, and the polymeric compounds on the other, and which are later mixed. Introducing a third constituent may have the result of modifying drastically the end properties of the coating
15 in which the pigment-polymer particles are incorporated.

In the present invention a process has been discovered in a surprising manner for the preparation of self-binding pigmentary particles, dry or in aqueous suspension or dispersion, containing at least one inorganic matter and at least one polymeric binder,
20 using a ball mill.

Firstly, this process is different from the simple mixing described in document WO 03/74786.

25 Secondly, the process according to the invention spares the skilled man in the art from using a third constituent during the preparation of the aqueous suspensions containing the inorganic matter and the binders, and during the co-grinding stage.

In addition, and in a surprising manner, the binders do not adhere and do not block the
30 mill, such that soiling of the equipment may be satisfactorily controlled.

Finally, another object of the invention resides in the self-binding pigmentary particles in the dry form obtained by the process according to the invention, containing at least one inorganic matter and at least one binder.

The term binder used in the present application refers to any natural or synthetic product of an organic nature, having binding properties. These binding properties, which increase the inter-particle cohesion forces of the initial mineral, are determined according to the method described in example 1 of the present application.

According to the object of the invention, the process for the preparation of self-binding pigmentary particles, dry or in aqueous suspension or dispersion, comprises the following stages:

10

- a) forming one or more aqueous suspensions of at least one inorganic matter and introducing it or them into a mill with a view to stage c),
- b) forming or taking one or more aqueous solutions or suspensions or emulsions of at least one binder and introducing it or them into a mill with a view to stage c),
- 15 c) co-grinding the aqueous suspension or suspensions obtained in stage a) with the aqueous solutions or suspensions or emulsions obtained in stage b) so as to obtain an aqueous suspension of self-binding pigmentary particles,
- d) possibly co-grinding the aqueous suspension obtained in stage c) with one or more aqueous solutions or suspensions or emulsions of at least one binder,
- 20 e) possibly drying the aqueous suspension obtained in stage c) or in stage d).

According to the invention, the aqueous suspension formed in stage a) is characterised in that it contains from 1 % to 80 % by dry weight of inorganic matter, and more preferentially from 15 % to 60 % by dry weight of inorganic matter.

25

The aqueous suspension formed in stage a) may contain one or more inorganic matter, notably metal oxides, hydroxides, sulphites, silicates and carbonates, such as calcium carbonate, dolomites, kaolin, talc, gypsum, titanium dioxide, satin white or aluminium trihydroxide and their mixtures. Preferentially it contains calcium carbonate, in a natural form or precipitated form, and more preferentially natural calcium carbonate, and very preferentially a natural calcium carbonate chosen from among chalk, marble, calcite or their mixtures.

30

According to the invention, the aqueous solution(s) or suspension(s) or emulsion(s) formed in stage b) are characterised in that they contain from 1 % to 50 % by weight of at least one binder, and more preferentially from 5 % to 20 % by weight of at least one binder.

5

The aqueous solution(s) or suspension(s) or emulsion(s) formed in stage b) are also characterised in that the binder is chosen from among the semi-crystalline latexes, and preferentially from among the emulsions of polyethylene waxes or copolymers in their neutralised polyethylene form with other monomer units such as acrylic acid or other
10 monomers or their mixtures, or from among the latexes in emulsion or solutions of soluble binders such as polyvinyl alcohol, polyvinyl acetate, starch, casein, proteins, carboxymethyl cellulose (CMC), ethyl hydroxyethyl cellulose (EHEC) or others, or their mixtures.

15 According to this variant, the semi-crystalline latexes are preferentially chosen from among the emulsions of polyethylene wax or the copolymers in their neutralised polyethylene form with other monomer units such as acrylic acid or other monomers or their mixtures, and the latexes in emulsion are preferentially chosen from among the copolymers of acrylic esters.

20

According to stage c) of the process according to the invention, the aqueous suspension(s) obtained in stage a) and the aqueous solution(s) or suspension(s) or emulsion(s) obtained in stage b) are then co-ground in order to obtain an aqueous suspension of self-binding pigmentary particles comprising at least one inorganic matter
25 and at least one binder.

According to stage d) of the process according to the invention, the aqueous suspension of self-binding pigmentary particles obtained in stage c) is then co-ground with one or more aqueous solution(s) or suspension(s) or emulsion(s) comprising at least one binder.

30

The Applicant has been able to observe that the binders adsorb to the surface of the mineral matter, thus creating chemical and physical bonds characteristic of self-binding particles, without having to use a dispersing agent or a third additive, as is illustrated by the figures of the different examples.

The co-grinding process is undertaken by all the techniques well known to the skilled man in the art.

- 5 According to the invention, the aqueous suspension obtained in stage c) or in stage d) is characterised in that the ratio between the inorganic matter and the binders contained in the suspension obtained is between 99 and 1 expressed as weight proportions, and preferentially between 70 and 30 expressed as weight proportions.
- 10 Preferentially, the composition of the said aqueous suspension is between 5 % and 80 % by weight of inorganic matter, between 1 % and 30 % by weight of binders, and between 19 % and 94 % by weight of water. More preferentially, the said aqueous suspension contains between 20 % and 40 % by weight of inorganic matter, between 5 % and 20 % by weight of binders, and between 40 % and 75 % by weight of water.

15

In addition, according to a variant of the process according to the invention, a preferential form of the aqueous suspension formed in stage c) or in stage d) is characterised in that the self-binding pigmentary particles have an average particle diameter of between 0.1 μm and 10 μm , and preferentially between 0.1 μm and 2 μm , measured using a

20 MasterSizer™ S granulometer sold by the company MALVERN.

This aqueous suspension or dispersion obtained in stage c) of the process according to the invention is self-binding, as is shown by example 1.

- 25 A possible variation of the process according the invention is characterised in that, after stage c) or possibly stage d), the two stages:
- f) Increasing the concentration of the aqueous suspension obtained at stage c) or d) through thermal or mechanical concentration;
 - g) Dispersing the aqueous suspension obtained at stage f) through using at least one
- 30 dispersing agent and/or at least one wetting agent.

According to this variant, the said dispersing agent or agents are selected from among the acrylic or vinylic or allyl polymers and/or copolymers, such as for example homopolymers or copolymers, in their totally acid or partially neutralised or totally

neutralised form, using neutralisation agents containing monovalent or polyvalent cations or amines or their mixtures, of at least one of the monomers such as the acrylic and/or methacrylic, itaconic, crotonic, fumaric acids, maleic or isocrotonic acid, aconitic, mesaconic, sinapic, undecylenic anhydrides, angelic acid, and/or their respective esters, such as the acrylates and methacrylates of alkyl, of aryl, of alkylaryl, of arylalkyl and in particular ethyl acrylate, butyl acrylate, methyl methacrylate, acrylamido methyl propane sulphonic acid, acrylamide and/or methacrylamide, acrylate phosphate of glycol ethylene, methacrylate phosphate of glycol ethylene, acrylate phosphate of glycol propylene acrylate, methacrylate phosphate of glycol propylene, methacrylamido propyl trimethyl ammonium chloride or sulphate, ethyl chloride or ammonium trimethyl methacrylate sulphate, together with their acrylate and acrylamide counterparts, whether or not quaternised, and/or dimethyldiallyl chloride, vinylpyrrolidone, vinylcaprolactame, diisobutylene, vinyl acetate, styrene, alpha-methyl-styrene, sodium sulfonate styrene, vinylmethylether, and allylamine.

15

This or these dispersing agents can also be chosen from among at least one of the said monomers or their mixtures, polymerised in the presence of at least one mineral matter.

In addition, it should be noted that the optimisation of the molecular weight of this or these dispersing agents depends on their chemical nature.

In addition, the said aqueous dispersion of self-binding pigmentary particles contains between 0.01 % and 2 % by weight of dispersing agents.

25 According to this variant, the aqueous dispersion of self-binding pigmentary particles contains between 0.01 % and 5 % by weight of wetting agents.

In a final stage e) of the process according to the invention, the aqueous suspension or dispersion obtained in stage c) or in stage d) may be dried, so as to obtain self-binding pigmentary particles in a dry form, containing at least one inorganic matter and at least one binder, and possibly at least one dispersing agent and at least one wetting agent.

This stage is accomplished by all known drying methods, and preferentially by a method of drying by spraying in a diluted medium.

In the process according to the invention, the result of stage e) consists in self-binding pigmentary particles in a dry form, containing at least one inorganic matter and at least one binder, characterised in that they contain between 70 % and 97.5 % by weight of
5 inorganic matter, and between 2.5 % and 30 % by weight of binders, and more preferentially between 85 % and 95 % by weight of inorganic matter and between 5 % and 15 % by weight of binders.

In addition, in a variant and according to a preferred form, the average diameter of the
10 said self-binding pigmentary particles is between 5 μm and 100 μm , and more preferentially between 10 μm and 30 μm , measured using a MasterSizer™ S granulometer sold by the company MALVERN.

The invention is now illustrated through examples which cannot limit its scope.
15

Example 1

This example concerns the process for preparing self-binding pigmentary particles in an
20 aqueous suspension from marble and two suspensions of binders.

To accomplish this, the first stage a) of the process consists in forming an aqueous suspension of 1000 grams by dry weight of marble having an average particle diameter of 0.8 μm by putting the marble into suspension in water at a dry matter content by weight
25 equal to 20 %.

Stage b) of the process is this accomplished by diluting an aqueous suspension of binder Acronal™ S728 sold by the company BASF up to a dry matter content by weight equal to 20 %.
30

Stage c) is accomplished by the successive introduction of the marble suspension and the binder suspension in a mill of the Dyno-Mill™ type with a fixed cylinder, a rotating pulser, the grinding body of which consists in glass balls with a diameter of between 1.0 mm and 1.4 mm.

After 16 minutes' grinding, stage d) is continued through the addition into the mill of a second aqueous suspension of binder obtained by dilution, up to a dry matter content by weight equal to 20 % of Polygen™ WE4 sold by the company BASF.

- 5 The total volume occupied by the grinding body is equal to 460 cm^3 while its weight is equal to 820 g.

The grinding chamber has a volume of 600 cm^3 .

The circumferential speed of the mill is 10 m.s^{-1} .

The calcium carbonate suspension is recycled at a rate of 33 litres/hour.

- 10 The temperature during each grinding test is maintained at approximately 25°C .

On conclusion of the grinding (85 minutes) a sample of the obtained suspension of self-binding pigmentary particles is removed in a flask. The granulometry of the suspension is measured using a MasterSizer™ S granulometer sold by the company MALVERN™ and

- 15 is such that 85 % of the particles have an average diameter of less than or equal to $1 \mu\text{m}$.

The product thus obtained is an aqueous suspension of self-binding pigmentary particles having a dry matter by weight content of calcium carbonate equal to 20 %, an average particle diameter equal to $0.5 \mu\text{m}$ measured using a MasterSizer™ S granulometer, and a
20 marble/Acronal™ S728/Polygen™ WE4 ratio equal to 100/9.5/0.5 by dry matter weight proportions.

- In this example, the illustration of the difference between the mineral-self-binding pigmentary particles binder pair on the one hand, and for a simple mixture on the other
25 hand, is illustrated using a differential thermal analysis machine (ATD) TGA/SDTA 851e, sold by the company METTLER TOLEDO™. The heating conditions being: a rise in temperature of 5°C per minute, from 25°C to 350°C .

- In comparison, the same measurements were made on the pure products (marble and
30 binder).

Figure 1 illustrates the difference between the mineral-self-binding pigmentary particles binder pair according to the invention, and a simple mineral-binder mixture

To demonstrate the suitability for the self-binding character of the pigmentary particles thus obtained, tablets were formulated using a membrane filtration process.

5 A machine of the high-pressure filter press type is used, manufactured from a hollow steel tube. The said tube is closed at the top by a lid and contains the filtration membrane at the bottom.

A volume of 80 ml is then introduced of either a suspension containing only the inorganic matter (which is used to manufacture the reference samples), or of a suspension
10 according to the invention (which is used to manufacture the samples for testing).

A constant pressure of 15 bar is then applied, which enables the water to be eliminated, until a tablet 20 mm thick is obtained.

15 The samples are then dried in free air for 1 week.

The device and method used are described in detail in the document "Modified calcium carbonate coatings with rapid absorption and extensive liquid uptake capacity" (Colloids and Surfaces A, 236 (1-3), 2003, pp. 91-102),

20

The quasi-cylindrical solid blocks of pigmentary particles were ground using a disk mill (Jean Wirtz, Phoenix 4000) in the form of disk-shaped samples of diameter 25 mm and of approximate thickness 15 mm. The procedure is described in the document "Fluid transport into porous coating structures: some novel findings" (Tappi Journal, 83 (5),
25 2000, pp. 77-78).

The samples obtained underwent a crush resistance test on a Zwick-Roell tension machine with a WN158988 control unit, using a rod/flat system (with a hemispherical end). The force of the cell is 20 kN.

30

The samples are crushed at a speed of $3 \text{ mm} \cdot \text{min}^{-1}$ over a length of 10 mm. The values of the force for a deformation of 2 mm are illustrated in figure 2 for this example and the following examples.

Figure 2 illustrates the self-binding power for the self-binding pigmentary particles according to the invention: measurement of the force in the crush test for a 2 mm deformation for:

- 5 - samples of a suspension of self-binding pigmentary particles according to the invention,
- samples formulated according to the method described in example 1 from an aqueous suspension containing only the mineral matter used in the invention (2)

10

Figure 2 shows clearly that the process according to the invention enables self-binding pigmentary particles to be obtained in which the inter-particle cohesive forces between the mineral particles are much higher than in the case of the initial mineral matter. This phenomenon is observed for example 1, but also for examples 2 to 4 which will be

15 described subsequently.

Tables 1 and 1 bis indicate the granulometric distribution of the particles according to the invention, and of the initial mineral particles.

Size of particles (μm)	Quantity of particles by volume (%) (1)	Quantity of particles by volume (%) (2)
< 71	100	100
< 45	100	100
< 25	100	100
< 10	100	99
< 5	100	96
< 2	98	84
< 1	85	59
< 0.7	71	
< 0.5	52	24
< 0.2	4	6
< 0.1	0	1

Table 1: granulometric distribution as measured using a MasterSizer™ S granulometer sold by the company MALVERN™ in the case of the suspension of self-binding pigmentary particles obtained using the process according to the invention (1), using a Sedigraph™ 5100 sold by the company MICROMERITICS in the case of a suspension
5 of initial inorganic matter (2).

	1	2
D ₅₀ (%)	0.48	0.85
D ₉₀ (%)	1,21	-

Table 1 bis: value of the parameters D₅₀ (%) and D₉₀ (%) (diameter measurements for which respectively 50 % and 90 % by volume of the particles having a diameter of less than or equal to this value) for:

- 15 - the self-binding pigmentary particles obtained using the process according to the invention (1)
 - the initial inorganic matter (2)

Tables 1 and 1 bis demonstrate a notable reduction of the particle sizes, in the case of the
20 self-binding pigmentary particles obtained according to the invention, relative to the initial inorganic matter.

Example 2

25

This example concerns the process for preparing self-binding pigmentary particles in an aqueous suspension from marble and from a styrene-butadiene binder.

To accomplish this, the first stage a) of the process consists in forming an aqueous
30 suspension of marble having an average particle diameter of 0.85 µm by putting the marble into suspension in water at a dry matter content by weight equal to 20 %.

For the second stage b) of the process, an aqueous suspension of binder DL 966 of DOW CHEMICALS is used at a content by weight of 50 %.

Stage c) of the process is then undertaken by co-grinding the marble suspension obtained in stage a) with the suspension of binder obtained in stage b) with the same equipment as that used in example 1.

- 5 On conclusion of the grinding (30 minutes) a sample of the obtained suspension of self-binding pigmentary particles is removed in a flask. The granulometry of the suspension is measured using a MasterSizer™ S granulometer sold by the company MALVERN™ and is such that 75 % of the particles have an average diameter of less than or equal to 1 µm.
- 10 The product thus obtained is an aqueous suspension of self-binding pigmentary particles having a dry matter by weight content of calcium carbonate equal to 21 %, an average particle diameter equal to 0.65 µm measured using a MasterSizer™ S granulometer sold by the company MALVERN™ and a calcium carbonate/binder ratio equal to 100/10 by weight proportions.

15

The binding power of the said particles was measured by a crush test according to the method described in example 1, and is illustrated in figure 2. The latter shows that the process according to the invention enables self-binding pigmentary particles to be obtained in which the inter-particular cohesive forces between the mineral particles are

- 20 much higher than in the case of the initial mineral matter.

Tables 2 and 2 bis indicate the granulometric distribution of the particles according to the invention, and of the initial mineral particles.

Size of particles (µm)	Quantity of particles by volume (%) (1)	Quantity of particles by volume (%) (2)
< 71	100	100
< 45	100	100
< 25	100	100
< 10	100	99
< 5	100	96
< 2	98	84
< 1	75	59

< 0.7	54	
< 0.5	35	24
< 0.2	5	6
< 0.1	1	1

Table 2: granulometric distribution as measured using a MasterSizer™ S granulometer sold by the company MALVERN™ in the case of the suspension of self-binding pigmentary particles obtained using the process according to the invention (1), using a Sedigraph™ 5100 sold by the company MICROMERITICS in the case of a suspension of initial inorganic matter (2)

	1	2
D ₅₀ (%)	0.65	0.85
D ₉₀ (%)	2,00	

- Table 2 bis:** value of the parameters D₅₀ (%) and D₉₀ (%) (diameter measurements for which respectively 50 % and 90 % by volume of the particles having a diameter of less than or equal to this value) for:
- the self-binding pigmentary particles obtained using the process according to the invention (1)
 - the initial inorganic matter (2)

Tables 2 and 2 bis demonstrate a notable reduction of the particle sizes, in the case of the self-binding pigmentary particles obtained according to the invention, relative to the initial inorganic matter.

Example 3

This example concerns the process for preparing self-binding pigmentary particles in an aqueous suspension from precipitated calcium carbonate (PCC) and two suspensions of binders.

To accomplish this, the first stage a) of the process consists in forming an aqueous suspension of precipitated calcium carbonate having an average diameter of 1.8 μm by putting the precipitated calcium carbonate into suspension in water at a dry matter content by weight equal to 20 %.

5

For the second stage b) of the process, use is made of a first aqueous suspension of Acronal™ S728 binder sold by the company BASF at a dry matter content by weight equal to 20 %, and a second aqueous suspension of Polygen™ WE4 binder sold by the company BASF at a dry matter content by weight equal to 20 %.

10

The three suspensions are then co-ground with the same equipment as that of example 1.

On conclusion of the grinding (30 minutes) a sample of the obtained suspension of self-binding pigmentary particles is removed in a flask. The granulometry of the suspension is measured using a MasterSizer™ S granulometer sold by the company MALVERN™ and is such that 83 % of the particles have an average diameter of less than or equal to 1 μm .

The product thus obtained is an aqueous suspension of self-binding pigmentary particles having a dry matter by weight content of precipitated calcium carbonate equal to 20 %, an average particle diameter equal to 0.53 μm measured using a MasterSizer™ S granulometer sold by the company MALVERN™ and a PCC/Acronal™ S728/Polygen™ WE4 ratio equal to 100/9.5/0.5 by dry matter weight proportions.

The binding power of the said particles was measured by a crush test according to the method described in example 1, and is illustrated in figure 2. The latter shows that the process according to the invention enables self-binding pigmentary particles to be obtained in which the inter-particle cohesive forces between the mineral particles are much higher than in the case of the initial mineral matter.

Tables 3 and 3 bis indicate the granulometric distribution of the particles according to the invention, and of the initial mineral particles.

Size of particles (μm)	Quantity of particles by volume (%) (1)	Quantity of particles by volume (%) (2)
< 71	100	100
< 45	100	100
< 25	100	100
< 10	100	100
< 5	100	96
< 2	98	59
< 1	83	38
< 0.7	65	29
< 0.5	47	21
< 0.2	9	5
< 0.1	1	1

Table 3: granulometric distribution as measured using a MasterSizer™ S granulometer sold by the company MALVERN™ in the case of the suspension of self-binding pigmentary particles obtained using the process according to the invention (1), using a Sedigraph™ 5100 sold by the company MICROMERITICS in the case of a suspension of initial inorganic matter (2)

	1	2
D ₅₀ (%)	0.53	1.57
D ₉₀ (%)	2.00	6.0

Table 3 bis: value of the parameters D₅₀ (%) and D₉₀ (%) (diameter measurements for which respectively 50 % and 90 % by volume of the particles having a diameter of less than or equal to this value) for:

- the self-binding pigmentary particles obtained using the process according to the invention (1)
- the initial inorganic matter (2)

Tables 3 and 3 bis demonstrate a notable reduction of the particle sizes, in the case of the self-binding pigmentary particles obtained according to the invention, relative to the initial inorganic matter.

5

Example 4

This example concerns the process for preparing self-binding pigmentary particles in aqueous suspension from a mixture of talc and titanium dioxide and a solution of binders
10 obtained by mixing starch and polyvinyl alcohol.

To accomplish this, the first stage a) of the process according to the invention consists in producing an aqueous suspension of talc having an average diameter of 13 μm and of titanium dioxide having an average diameter of less than 0.2 μm , by putting in
15 suspension the talc and the titanium dioxide (in a 1:1 ratio by dry weight) in water at a dry matter weight content equal to 48 %.

Stage b) of the process according to the invention is undertaken by diluting an aqueous suspension of polyvinyl alcohol MowiolTM 4-88 sold by the company OMYA Peralta
20 until a dry matter content by weight equal to 34 % is reached, whilst stirring for 20 minutes, at a temperature of 90 °C, and whilst preparing a solution of starch at a dry matter content by weight equal to 22 %, whilst stirring for 20 minutes, at a temperature of 90 °C.

25 Following this, the resulting suspension is co-ground with the same equipment as in example 1.

On conclusion of the grinding (30 minutes) a sample of the obtained suspension of self-binding pigmentary particles is removed in a flask. The granulometry of the suspension is
30 measured using a MasterSizerTM S granulometer sold by the company MALVERNTM and is such that 28 % of the particles have an average diameter of less than or equal to 1 μm .

The product thus obtained is an aqueous suspension of self-binding pigmentary particles having a dry matter by weight content of talc and titanium dioxide equal to 37 %, an

average particle diameter equal to 46 μm measured using a MasterSizer™ S granulometer sold by the company MALVERN™ and a talc and titanium dioxide/polymeric binders ratio equal to 100/10 by weight proportions.

- 5 The binding power of the said particles was measured by a crush test according to the method described in example 1, and is illustrated in figure 2. The latter shows that the process according to the invention enables self-binding pigmentary particles to be obtained in which the inter-particle cohesive forces between the mineral particles are much higher than in the case of the initial mineral matter.

10

Tables 4 and 4 bis indicate the granulometric distribution of the particles according to the invention, and of the initial mineral particles.

Size of particles (μm)	Quantity of particles by volume (%) (1)	Quantity of particles by volume (%) (2)
< 71	100	99
< 45	97	91
< 25	86	70
< 10	54	41
< 5	37	32
< 2	29	27
< 1	28	25
< 0.7	27	23
< 0.5	24	20
< 0.2	5	6
< 0.1		1

15

Table 4: granulometric distribution as measured using a MasterSizer™ S granulometer sold by the company MALVERN™ in the case of the suspension of self-binding pigmentary particles obtained using the process according to the invention (1), using a

Sedigraph™ 5100 sold by the company MICROMERITICS in the case of a suspension of initial inorganic matter (2)

5

	1	2
D ₅₀ (%)	8.9	14.3
D ₉₀ (%)	9.0	15.0

Table 4 bis: value of the parameters D₅₀ (%) and D₉₀ (%) (diameter measurements for which respectively 50 % and 90 % by volume of the particles having a diameter of less than or equal to this value) for:

- 10 - the self-binding pigmentary particles obtained using the process according to the invention (1)
- the initial inorganic matter (2)

Tables 4 and 4 bis demonstrate a notable reduction of the particle sizes, in the case of the self-binding pigmentary particles obtained according to the invention, relative to the initial inorganic matter.

Example 5

20

This example illustrates a variant of the process of preparation according to the invention for pigmentary self-linking particles in aqueous suspension from marble and from two binding agents in suspension.

25 To do this, we produce with the same material and the same operating conditions as in example 1, the aqueous suspension of self-binding pigmentary particles from example 1, having a content in weight of dry material of calcium carbonate equal to 20%, an average particle diameter of 0.50 µm as measured by a MasterSizer™ S, and a marble/Acronal™ S728/Polygen™ WE4 equal to 100/9, 5/0, 5 in parts in dry material weight.

30

Once this aqueous suspension of self-binding pigmentary particles is obtained, it is put in a Rouan YXY centrifuge rotating at 5,500 rpm so as to increase its dry material concentration.

- 5 After 6 minutes in the centrifuge, the resulting aqueous suspension has 58% dry material content.

Once obtained, this concentrated aqueous suspension of self-binding pigmentary particles is dispersed using a Pendraulik™ agitator at 300 rpm and adding 0.5% dry weight of the
 10 dry weight of pigmentary particles of a wetting agent, styrene copolymer / butyl acrylate / methacrylic acid / acrylic acid and 0.1% dry weight of the dry weight of pigmentary particles of a dispersing agent, acrylic acid copolymer / maleic anhydride, then the quantity of water needed to obtain a 55% concentration of dry material.

- 15 The resulting Brookfield™ viscosity figure is 106 mPa.s at 100 rpm.

Example 6

- 20 This example again illustrates another variant of the process according to the invention.

To do this, we produce with the same material and the same operating conditions as in example 1, the aqueous suspension of self-binding pigmentary particles from example 1, having a content in weight of dry material of calcium carbonate equal to 20%, an average
 25 particle diameter of 0.50 µm as measured by a MasterSizer™ S, and a marble/Acronal™ S728/Polygen™ WE4 equal to 100/9, 5/0, 5 in parts in dry material weight.

Once obtained this suspension of self-binding pigmentary particles, a filter press is used to raise the suspension's dry material concentration up to 65.4%.

30

Once obtained this concentrated aqueous suspension of self-binding pigmentary particles, we disperse it using a Pendraulik™ agitator at an even speed of 3,000 rpm and consecutively adding 0.17% in dry weight of the Tamol™ NN9104 wetting agent and

0.59% in dry weight of the Coatex P70 dispersing agent, in dry weight terms of pigmentary particles.

After 14 days storage the Brookfield™ viscosity index is 1630 mPa.s at 100 rpm.

CLAIMS

1. A process for the preparation of self-binding pigmentary particles, dry or in aqueous suspension or dispersion, comprising the following stages:
 - a) forming one or more aqueous suspensions of at least one inorganic matter and introducing it or them into a mill with a view to stage c)
 - b) forming or taking one or more aqueous solutions or suspensions or emulsions of at least one binder and introducing it or them into a mill with a view to stage c)
 - c) co-grinding the aqueous suspension or suspensions obtained in stage a) with the aqueous solutions or suspensions or emulsions obtained in stage b) so as to obtain an aqueous suspension of self-binding pigmentary particles
 - d) possibly co-grinding the aqueous suspension obtained in stage c) with one or more aqueous solutions or suspensions or emulsions of at least one binder
 - e) possibly drying the aqueous suspension obtained in stage c) or in stage d)
2. A process according to claim 1 characterised in that the aqueous suspension or suspensions of inorganic matter formed in stage a) contain from 1 % to 80 % by dry weight of inorganic matter.
3. A process according to claim 2 characterised in that the aqueous suspension or suspensions of inorganic matter formed in stage a) contain from 15 % to 60 % by dry weight of inorganic matter.
4. A process according to one of the claims 1 to 3 characterised in that the said aqueous suspension or suspensions of inorganic matter formed in stage a) contain one or more inorganic matter.
5. A process according to claim 4 characterised in that the said inorganic matter are chosen from among the metallic oxides, the hydroxides, the sulphites, the silicates and the carbonates, such as calcium carbonate, the dolomites, kaolin, talc, gypsum, titanium dioxide, satin white or aluminium trihydroxide and their mixtures.

6. A process according to claim 5 characterised in that the said inorganic matter is chosen from among the calcium carbonates in the natural form or in the precipitated form or their mixtures.
- 5 7. A process according to claim 6 characterised in that the said inorganic matter is a natural calcium carbonate chosen from among chalk, marble, calcite, or their mixtures.
8. A process according to one of the claims 1 to 7 characterised in that the aqueous
10 solutions or suspensions or emulsions of at least one binder formed in stage b) contain from 1 % to 50 % by weight of at least one binder, and more preferentially from 5 % to 20 % by weight of at least one binder.
9. A process according to one of the claims 1 to 8 characterised in that the binder or
15 binders of stage b are chosen from among the semi-crystalline latexes, or from among the latexes in emulsion or the solutions of soluble binders such as polyvinyl alcohol, polyvinyl acetate, starch, casein, proteins, carboxymethyl cellulose (CMC), ethyl hydroxyethyl cellulose (EHEC), or their mixtures.
- 20 10. A process according to claim 9 characterised in that the semi-crystalline latexes are preferentially chosen from among the emulsions of polyethylene waxes or copolymers in their neutralised form of polyethylene with other monomer units such as acrylic acid or other monomers or their mixtures.
- 25 11. A process according to claim 9 characterised in that the emulsion latexes are chosen from among the copolymers of acrylic esters.
12. A process according to one of the claims 1 to 11 characterised in that the
30 suspension formed in stage c) has a ratio between inorganic matter and binders contained in the suspension obtained between 99 and 1 expressed in weight proportions.

13. A process according to claim 12 characterised in that the ratio between the inorganic matter and the binders contained in the suspension obtained is between 70 and 30 expressed as weight proportions.
- 5 14. A process according to one of the claims 1 to 13 characterised in that the self-binding pigmentary particles thus formed have an average particle diameter of between 0.1 μm and 10 μm measured using a MasterSizer™ S granulometer sold by the company MALVERN.
- 10 15. A process according to claim 14 characterised in that the self-binding pigmentary particles thus formed have an average particle diameter of between 0.1 μm and 2 μm measured using a MasterSizer™ S granulometer sold by the company MALVERN.
- 15 16. The procedure according to the one of the claims 1 to 15 is characterised in that it includes the following stages:
- a) forming one or more aqueous suspensions containing at least one inorganic material in a grinder in view of stage c)
 - 20 b) forming or taking one or more solutions or suspensions or emulsions containing at least one binder in a grinder in view of stage c)
 - c) co-grinding the suspension or suspensions obtained at stage a) with the solutions or aqueous suspensions or emulsions obtained at stage b) so as to
25 obtain an aqueous suspension of self-binding pigmentary particles
 - d) possibly co-grinding the aqueous suspension obtained at stage c) with one or more solutions or aqueous suspensions or emulsions of at least one binder
 - 30 f) increasing the concentration of the aqueous suspension obtained at stage c) or d) through thermal or mechanical concentration;
 - g) dispersing the aqueous suspension obtained at stage f) through using at least one dispersing agent and/or at least one wetting agent.

17. A process according to claim 16 characterised in that the dispersing agent or agents are chosen from among polymers and/or acrylic or vinylic or allylic copolymers, such as homopolymers or copolymers in their totally acidic or partially or totally neutralised forms by neutralising agents containing monovalent or polyvalent cations or amines or their mixtures, from at least one of the monomers such as the acrylic and/or methacrylic, itaconic, crotonic, fumaric acids, the maleic anhydride or isocrotonic, aconitic, mesaconic, sinapic, undecylenic acid, angelic acid and/or their respective esters such as the acrylates or methacrylates of alkyl, aryl, alkylaryl, arylalkyl and in particular ethyl acrylate, butyl acrylate, methyl methacrylate, sofonic acrylamido methyl propane acid, acrylamide and/or methacrylamide, carylate phosphate of glycol ethylene. methacrylate phosphate of glycol ethylene, acrylate phosphate of glycol propylene, methacrylate phosphate of glycol propylene, chlorine or ammonium trimethyl propyl methacrylamid sulphate, as well as their acrylate and acrylamide equivalents, quaternised or not, and/or dimethyldiallyl chlorate, vinylpyrrolidone, vinylcaprolactame, diisobutylene, vinyl acetate, styrene, alpha-methyl-styrene, styrene sodium sulfonate, vinylmethylether, allyllamine or chosen from at least one of the said monomers or their mixtures, polymerised in the presence of at least one mineral material.
18. A process according to one of the claims 16 or 17 characterised in that from 0.01 % to 2 % by weight of at least one dispersing agent is added.
19. A process according to claim 16 characterised in that from 0.01 % to 5 % by weight of at least one wetting agent is added.
20. An aqueous suspension of self-binding pigmentary particles containing at least one inorganic matter and at least one binder characterised in that it is obtained by the process according to one of the claims 1 to 15.
21. An aqueous suspension of self-binding pigmentary particles containing at least one inorganic matter and at least one binder characterised in that it is obtained by the process according to one of the claims 1 to 15, characterised in that it is self-binding.

22. An aqueous suspension of self-binding pigmentary particles containing at least one inorganic matter and at least one binder according to one of the claims 20 or 21 characterised in that it contains between 5 % and 80 % by weight of inorganic matter, between 1 % and 30 % by weight of binders, and between 19 % and 94 % by weight of water, and preferentially, in that it contains between 20 % and 40 % by weight of inorganic matter, between 5 % and 20 % by weight of binders, and between 40 % and 75 % by weight of water.
23. An aqueous dispersion of self-binding pigmentary particles containing at least one inorganic matter and at least one binder characterised in that it is obtained by the process according to one of the claims 16 to 19.
24. An aqueous dispersion of self-binding pigmentary particles containing at least one inorganic matter and at least one binder characterised in that it is obtained by the process according to one of the claims 16 to 19, characterised in that it is self-binding.
25. An aqueous dispersion of self-binding pigmentary particles containing at least one inorganic matter and at least one binder according to one of the claims 23 or 24, characterised in that it contains between 5 % and 80 % by weight of inorganic matter, between 1 % and 30 % by weight of binders, between 19 % and 94 % by weight of water, between 0.01 % and 2 % by weight of at least one dispersing agent and/or between 0.01 % and 5 % by weight of at least one wetting agent, and preferentially in that it contains between 20 % and 40 % by weight of inorganic matter, between 5 % and 20 % by weight of binders, between 40 % and 75 % by weight of water, between 0.01 % and 2 % by weight of at least one dispersing agent and/or between 0.01 % and 5 % by weight of at least one wetting agent.
26. A process according to one of the claims 1 to 15 characterised in that the self-binding pigmentary particles formed in stage e) contain from 70 % to 97.5 % by weight of at least one inorganic matter and from 2.5 % to 30 % by weight of at least one binder.

27. A process according to claim 26 characterised in that the self-binding pigmentary particles formed in stage e) contain from 85 % to 95 % by weight of at least one inorganic matter and from 5 % to 15 % by weight of at least one binder.
- 5 28. A process according to one of the claims 1 to 15 and according to one of the claims 26 or 27 characterised in that the average diameter of the self-binding pigmentary particles formed in stage e) is between 5 μm and 100 μm as measured using a MasterSizer™ S granulometer sold by the company MALVERN.
- 10 29. A process according to claim 28 characterised in that the average diameter of the self-binding pigmentary particles formed in stage e) is between 10 μm and 30 μm as measured using a MasterSizer™ S granulometer sold by the company MALVERN.
30. Self-Binding pigmentary particles, containing at least one inorganic matter and at
15 least one binder, obtained by the process according to one of the claims 1 to 19 and 26 to 29, characterised in that they contain from 70 % to 97.5 % by weight of at least one inorganic matter and from 2.5 % to 30 % by weight of at least one binder, and preferentially in that they contain between 85 % and 95 % by weight of at least one inorganic matter and from 5 % to 15 % by weight of at least one binder.