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(54) **Titre** : PROCEDE POUR LA PREPARATION DE PARTICULES PIGMENTAIRES AUTO-LIANTES METTANT EN JEU DES COPOLYMERES ACRYLIQUES A STRUCTURE EN PEIGNE COMPORTANT DES GROUPES HYDROPHOBES EN TANT QU'AGENTS DE COUPLAGE, PARTICULES PIGMENTAIRES AUTO- LIANTES ET LEURS UTILISATIONS

(54) **Title**: PROCESS TO PREPARE SELF-BINDING PIGMENT PARTICLES IMPLEMENTING ACRYLIC COMB COPOLYMERS WITH HYDROPHOBIC GROUPS AS COUPLING AGENTS, SELF BINDING PIGMENT PARTICLES AND USES THEREOF

(57) **Abrégé/Abstract**:

The present invention relates to a process to prepare self-binding pigment particles comprising at least one step a) of grinding one or more binders and one or more mineral materials in an aqueous environment to obtain a suspension, characterised in that, prior to and/or during step a), a copolymer is added in the form of an aqueous solution, said copolymer resulting from the polymerisation of: 2.1) at least one anionic monomer that is an alkene; 2.2) at least one oxyalkylated monomer that is an alkene, wherein the oxyalkyl group has a terminal hydrophobic alkyl, aryl, alkyl aryl or aryl alkyl group having 10 to 32 carbon atoms; 2.3) optionally, at least one other monomer that is an acrylic ester, a preferred acrylic ester being ethyl acrylate, and/or an unsaturated amide, a preferred unsaturated amide being acrylamide, as well as to the products obtained by this process, and uses of these products.

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(54) **Title**: PROCESS TO PREPARE SELF-BINDING PIGMENT PARTICLES IMPLEMENTING ACRYLIC COMB COPOLYMERS WITH HYDROPHOBIC GROUPS AS COUPLING AGENTS, SELF BINDING PIGMENT PARTICLES AND USES THEREOF

(57) **Abstract**: The present invention relates to a process to prepare self-binding pigment particles comprising at least one step a) of grinding one or more binders and one or more mineral materials in an aqueous environment to obtain a suspension, characterised in that, prior to and/or during step a), a copolymer is added in the form of an aqueous solution, said copolymer resulting from the polymerisation of: 2.1) at least one anionic monomer that is an alkene; 2.2) at least one oxyalkylated monomer that is an alkene, wherein the oxyalkyl group has a terminal hydrophobic alkyl, aryl, alkyl aryl or aryl alkyl group having 10 to 32 carbon atoms; 2.3) optionally, at least one other monomer that is an acrylic ester, a preferred acrylic ester being ethyl acrylate, and/or an unsaturated amide, a preferred unsaturated amide being acrylamide, as well as to the products obtained by this process, and uses of these products.

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Process to prepare self-binding pigment particles implementing acrylic comb copolymers with hydrophobic groups as coupling agents, self binding pigment particles and uses thereof

Binders and mineral materials are among the main constituents of paper coating colours. The former, generally latex-based and in the form of aqueous suspensions or dispersions, provide the necessary adhesion and cohesion between the elements forming the paper coating. The latter, commonly calcium carbonate, may provide improvements in paper quality, notably relative to its optical properties.

The concept of self-binding pigment particles is known to industry: it refers to distinct, solid particles, formed of mineral material and binder that are intimately bound to one another. The internal cohesion forces are such as to provide the self-binding pigment particles with excellent mechanical stability. Such particles may be directly implemented in a variety of applications.

Implementing self-binding pigment particles avoids the logistic difficulties of handling mineral materials and binders separately, and further avoids the unwanted physical and chemical interactions developed in comparable mixtures of minerals and binders. Such issues are notably referred to in "Physical and Chemical Modifications in latex binders and their effects on the coating colour rheology" (Advanced Coating Fundamentals Symposium, San Diego, CA, USA, May 4-5, 2001, pp 108-123), which underlines the negative effects of implementing mixtures of calcium carbonate and styrene-butadiene latex binders.

Self-binding pigment particles are prepared by a process implementing at least one step of grinding mineral materials in the presence of binder, where grinding refers to an operation leading to a reduction in the particle size; the mineral materials in the self-binding pigment particles have a smaller diameter than the initial mineral material used to produce them. Such self-binding pigment particles and variations thereon are described in a number of documents, including WO 2006 008657, WO 2006 128814, and WO 2008 139292.

It has generally been remarked that the use of a “coupling agent”, such as an ethylene-acrylic acid Poligen™ WE 4, in addition to the mineral material and binder during the self-binding pigment particle production process, provides for improved self-binding character in the formed pigment particles. Indeed, such coupling agents are thought to facilitate the development of a strong adhesion of the binders, including binders of natural origin such as starch, proteins such as casein, cellulose and cellulosic derivatives such as ethylhydroxyethyl cellulose (EHEC) and/or carboxymethylcellulose (CMC), and synthetic binders such as polyvinyl acetate (PVA), acrylic, acrylic ester, acrylonitrile, styrene or styrene-acrylic binders, at the carbonate surface. Such binders may be in the form of a solution, a suspension or an emulsion, such as Hycar™ acrylic emulsions manufactured by Lubricol™.

WO 2006 008657 described a process co-grinding inorganic materials in the presence of binder in an aqueous environment. The self-binding character is evaluated based on a crushing test, performed on tablets formed of the co-ground material. Of the six examples provided, four of these (examples 1, 3, 5 and 6) implement a binder as well as Poligen™ WE 4 (commercialised by BASF™). Only examples 5 and 6 lead to final solids contents of the self-binding pigment particle suspension of greater than 50% by weight; to obtain a workable suspension viscosity at these solids, it is necessary to add a wetting agent and a dispersing agent.

WO 2006 128814 refers to the impact of such self-binding pigment particles (called “polymer-pigment hybrid”) on the properties of paper in which it is applied. Notably, an improvement of the optical properties, such as opacity, is observed. This document describes the formation of such self-binding pigment particles by grinding calcium carbonate, in an aqueous environment, with a styrene-acrylate binder as well as Poligen™ WE 4. However, none of the resulting suspensions of self-binding pigment particles obtained have a solids content of greater than 30% by weight.

Finally, WO 2008 139292 describes a process implementing a step of grinding a pigmentary material in the presence of binder, followed by the addition of a specified inverse emulsion; examples implementing Poligen™ WE 4 in addition to binder are ground with calcium carbonate at 20% solids content. Concentrating this suspension leads to a 40% solids content slurry.

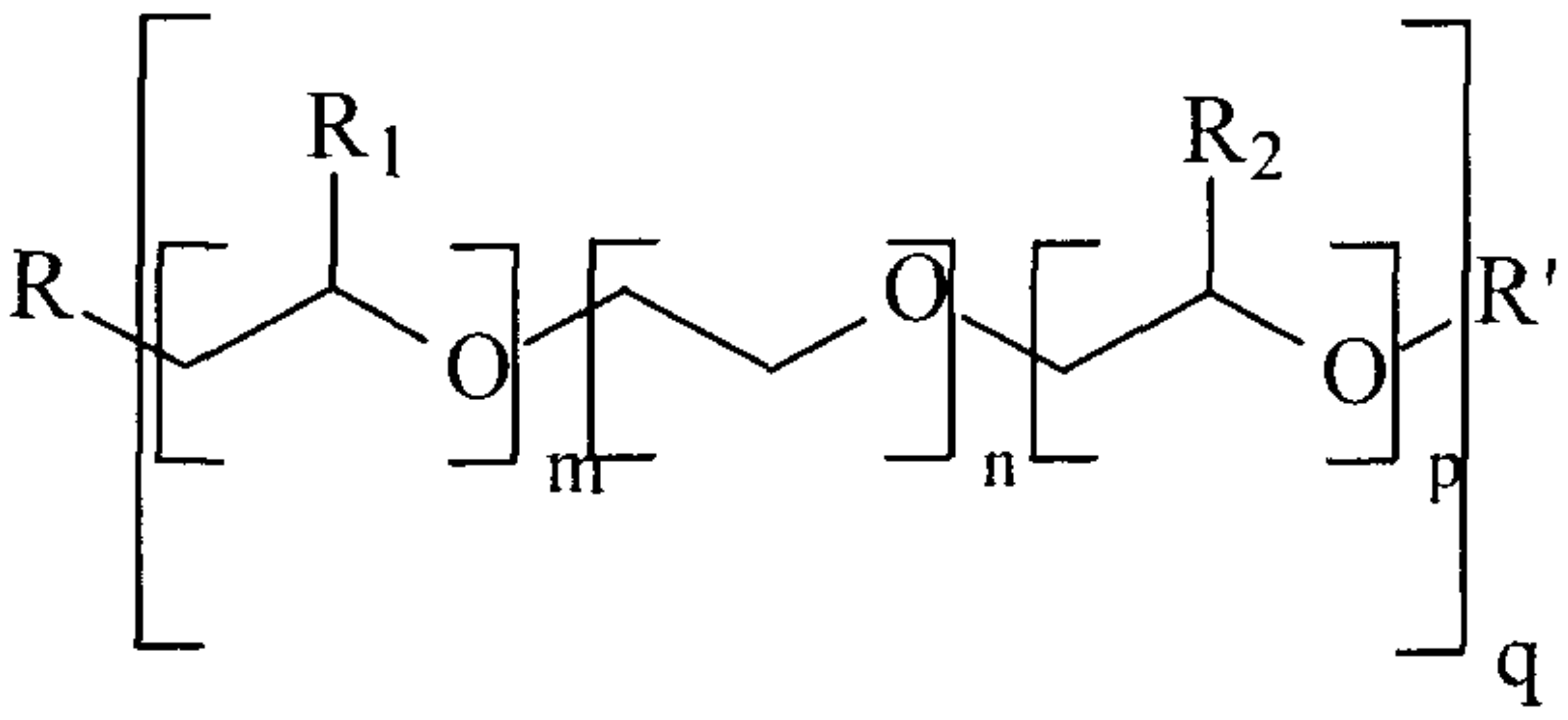
Improving the self-binding pigment particle production process remains of interest to the skilled man, and in his continued effort to do so, the Applicant has developed a process to prepare self-binding pigment particles comprising the following steps:

a) at least one step of grinding one or more binders and one or more mineral materials in an aqueous environment to obtain a suspension;
b) optionally, at least one step of concentrating the suspension obtained following step a), optionally in the presence of one or more dispersing aids;
c) optionally, drying the suspension obtained following steps a) or b) ;

characterised in that :

- prior to and/or during step a), a copolymer is added in the form of an aqueous solution, said copolymer resulting from the polymerisation of:

2.1) at least one anionic monomer that is an alkene;
2.2) at least one oxyalkylated monomer that is a monomer of Formula (I):



Formula (I)

wherein :

- m, n, p and q are whole numbers having a value of less than 150, and at least one of m, n, and p has a value of greater than 0, q has a value greater than or equal to 1;
- R represents a radical having a polymerisable alkene group,
- R_1 and R_2 are the same or different, and represent hydrogen or alkyl groups,

- R' represents an alkyl, aryl, alkyl aryl or aryl alkyl hydrocarbon chain having 10 to 32 carbon atoms;

2.3) optionally, at least one other monomer that is an acrylic ester.

For the purpose of the present Application, an anionic monomer is a monomer which, when introduced into an aqueous environment in the form of a monomer or as a polymerised monomer in a polymer, undergoes a dissociation to become anionic.

Implementing the inventive process with its selected coupling agent not only allows the skilled man to directly obtain a high solids content suspension, but the total organic content (TOC) of the aqueous phase of the suspension is similar or decreased when prepared by the process of the invention, relative to prior art processes.

For completeness, the Applicant would like to remark that WO 2004/041882 and WO 2004/0410883, which although mentioning similar copolymers as implemented herein, do not aim at resolving the technical problem of the present invention nor implement the specified copolymers in the process of the present invention.

Without wishing to be bound to any theory, the Applicant believes that the lower the TOC value of the suspension's aqueous phase, the greater the adhesive forces within the self-binding pigment particles suspended therein. The low TOC values suggest that only small quantities of binder, surfactants (serving to stabilise this binder) and coupling agent remain present in the aqueous phase. The result is that the process water can be reused with relative ease, which represents another advantage of the present invention.

In an embodiment which does not implement step b) of concentrating or step c) of drying, the process of the invention may lead directly to a high solids suspension of self-binding pigment particles. Indeed, the process of the invention makes it possible to avoid a mandatory concentration step.

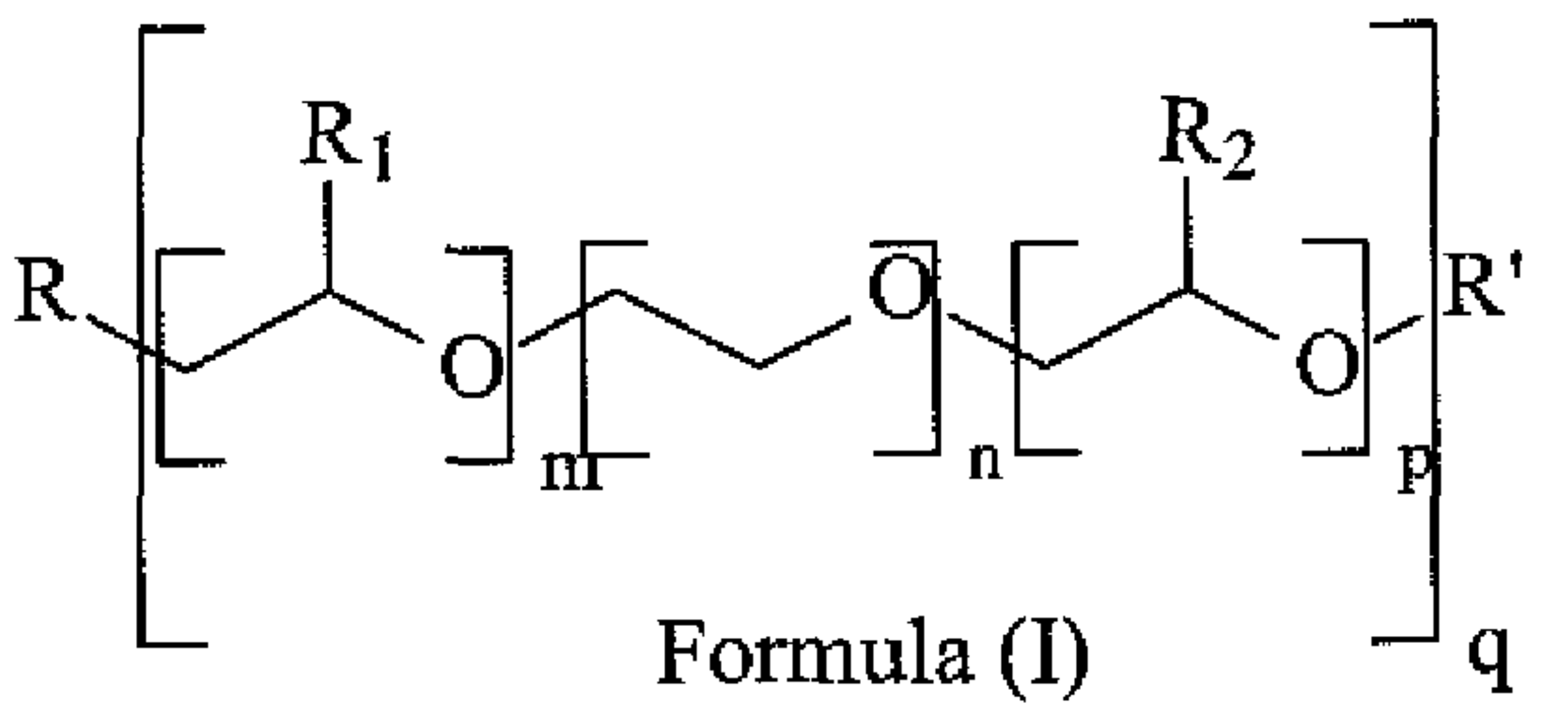
For the purpose of the present invention, concentrating refers to a step that increases the solids content of a suspension. Such a step may, for example, implement a filtration, centrifugation or any other means of mechanically concentrating.

In a preferred embodiment, the process of the invention implements the above copolymer such that said monomers are present in said copolymer in the following % by weight relative to the total copolymer weight:

2.1) from 5 to 95%, preferably from 50 to 95% and more preferably from 70 to 95% by weight of said anionic monomer(s);
2.2) from 5 to 95%, preferably from 5 to 50% and more preferably from 5 to 30% by weight of said oxyalkylated monomer(s);
2.3) from 0 to 30%, and preferably from 0 to 20% by weight of said other monomer(s).

In another preferred embodiment, said anionic monomer is selected from among acrylic acid, methacrylic acid and mixtures thereof.

In another preferred embodiment, said oxyalkylated monomer is a monomer of Formula (I):



Formula (I)

wherein :

- m, n, p and q are whole numbers having a value of less than 150, and at least one of m, n, and p has a value of greater than 0, q has a value greater than or equal to 1, preferably such that $15 \leq (m+n+p)q \leq 150$, more preferably such that $20 \leq (m+n+p)q \leq 60$, and even more preferably such that $25 \leq (m+n+p)q \leq 50$;
- R represents a radical having a polymerisable alkene group,
- R_1 and R_2 are the same or different, and represent hydrogen or alkyl groups,
- R' represents an alkyl, aryl, alkyl aryl or aryl alkyl hydrocarbon chain having 10 to 32 carbon atoms.

In such a case, it is preferred that R' be a branched hydrocarbon chain having 10 to 24 carbon atoms, preferably resulting from the condensation of linear alcohols according to the Guerbet reaction, R' being more preferably selected from among 2-hexyl-1-decanyl, 2-octyl-1-dodecanyl and mixtures thereof.

Alternatively, R' may be a polystyryl phenol, and preferably selected from among distyrylphenol, tristyrylphenol and mixtures thereof.

The radical R is preferably selected from among (a) hydrocarbon radicals such as vinyl radicals and/or allyl radicals, (b) radicals forming oxyalkyl esters such as radicals of: acrylic acid and/or methacrylic acid and/or maleic acid, (c) radicals forming N-oxyalkylurethanes, such as radicals of: acrylurethane and/or methacrylurethane and/or α-α' dimethyl-isopropenyl-benzylurethane and/or allylurethane, (d) radicals forming oxyalkyl ethers such as radicals forming vinyl oxyalkyl ethers and/or radicals forming allyl oxyalkyl ethers and/or radicals forming oxyalkylurethanes, (e) radicals forming oxyalkyl amides, (f) radicals forming oxyalkyl imides, and (g) mixtures thereof, and more preferably R is a radical forming an oxyalkyl methacrylic ester.

In another embodiment of the process of the present invention, said copolymer features a molar % of neutralisation of any acidic functional groups by one or more neutralising agent(s) of from 0 to 50 %, preferably from 0 to 35 %, and more preferably from 0 to 20 %. Preferred neutralisation agents include hydroxides of sodium, potassium, lithium or mixtures thereof.

In the case where step b) is implemented, said dispersing agent in any step b) may be an acrylic acid homo or copolymer.

In the case where step b) is implemented, said dispersing agent is preferably implemented in an amount of from 0.01 to 2 % by weight, relative to the dry weight of mineral material.

During step a), it is preferred that the solids content of the suspension being ground be from 1 to 80 %, and preferably from 15 to 60 % by dry weight relative to the total weight of said suspension.

The mineral material ground in step a) is preferably selected from among metal oxides such as titanium dioxide and/or aluminium trioxide, metal hydroxides such as aluminium trihydroxide, sulphites, silicates such as talc and/or kaolin clay and/or mica, carbonates such as calcium carbonate and/or dolomite, gypsum, satin white and mixtures thereof.

The binder of step a) is preferably selected from among (a) binders of natural origin such as starch, proteins such as casein, cellulose and cellulosic derivatives such as ethylhydroxyethyl cellulose (EHEC) and/or carboxymethylcellulose (CMC), and (b) synthetic binders, such as polyvinyl acetate (PVA), acrylic binders such as acrylic ester binders and/or acrylonitrile binders and/or styrene-acrylic binders, styrene binders, styrene-butadiene binders and butadiene binders, and (c) mixtures thereof.

During step a), it may be advantageous to employ a weight proportion of mineral material:binder contained in the suspension of between 99:1 and 1:99, and preferably of between 70:30 and 30:70.

Furthermore, it is generally preferred that said copolymer is implemented in an amount corresponding to 0.1 to 2 %, preferably 0.1 to 0.5 %, more preferably 0.1 to 0.3 % by dry weight relative to the dry weight of mineral material.

In another preferred embodiment, during any step b) from 0.01 to 2 % by weight, relative to the dry weight of mineral material, of at least one dispersing agent is added.

Another object of the present invention resides in self-binding pigment particles obtained by the process of the invention described here-above and their uses in plastics and paints. Such pigment particles can also find uses in paper industry.

EXAMPLES

In each of the following examples, grinding was performed in a Dyno-Mill™ grinder featuring a fixed cylinder and a rotating element, using zirconium-based grinding beads having an initial bead diameter of between 0.6 and 1 mm. In the grinding chamber of 1 400 cm^3, the total volume occupied by the grinding beads was 1 000 cm^3; their total weight was 2 700 g. The circumferential speed of the grinder was 10 m/s. The pigment suspension was recycled at a rate of 40 litres/hour. A 200 µm separation sieve was located at the exit of the Dyno-Mill™ in order to separate the suspension from the grinding beads. The temperature during each of the grinding trials was maintained at approximately 30°C.

For each of the tests below, polymer concentrations are given in % dry weight relative to the dry weight of mineral material. Unless otherwise indicated, all polymers implemented in the process of the invention are partially neutralised such that 10 mole % of their carboxylic sites are neutralised by sodium ions. Partial neutralisation of the polymer took place by adding sodium hydroxide at the moment of dispersant addition, in order to regulate the pH to between 8.5 and 10.

TOC measurement method

TOC measurements were made using a Total Organic Carbon Analyzer TOC-VCSH, commercialised by SHIMADZU™, equipped with an ASI-V sample injector and using TOC-Control V (SHIMADZU™) software.

Calibration of the instrument was undertaken using two solutions.

The first solution contained 1 000 ppm of total carbon and was prepared by introducing 2.125 g of potassium hydrogeno phthalate (previously dried at 110°C and cooled in a desiccator) in a 1 litre flask and thereafter adding water up to the 1 litre mark.

The second solution contained 1 000 ppm of inorganic carbon, and was prepared by introducing 4.41 g of sodium carbonate (previously dried at 280°C and cooled in a desiccator) and 3.5 g of sodium hydrogen carbonate in a 1 litre flask and thereafter adding water up to the 1 litre mark.

The calibration curves for 1 to 100 ppm of total carbon were prepared using the TC-100-23082006.cal procedure, and the curves for 0 to 50 ppm of inorganic carbon were prepared using the IC50-23082006.cal procedure.

For each of the tests below, filtrate samples for the TOC measurements were obtained by filtering the aqueous suspensions following grinding as described below. The amount of Total Organic Carbon (TOC) was then determined using the TOC-280820006.mand procedure.

Example 1

This example represents a process to prepare an aqueous suspension of self-binding pigment particles involving a step of grinding calcium carbonate, a binder and a coupling agent, as well as a concentration step followed by a dispersion step, unless otherwise indicated.

In each of the following tests, the listed coupling agent as well as 9.5 % by weight of a styrene-acrylate binder (commercialised by BASF™ under the trade name Acronal™ S 728) were added to an aqueous suspension of natural calcium carbonate (Norwegian marble) having a solids content of 17 % by dry weight.

Following grinding, the weight fractions of particles in suspension having a diameter of less than 1 and less than 2 μm (% < 1 μm and % < 2 μm, respectively) were determined using Sedigraph™ 5100 instrumentation commercialised by MICROMERITICS™.

Each suspension was then concentrated by filtration on a Büchner™ filter press to obtain a filter cake. The amount of Total Organic Carbon in the collected water (filtrate) was determined according to the method described hereabove.

The obtained filter cakes were subsequently dispersed using the listed dispersing agent(s) in order to obtain a suspension having a solids content of approximately 50 % by weight.

The Brookfield™ viscosities of the obtained suspensions at 25°C under 10 and 100 rpm were determined at time $t = 0$ ($\mu_{10\ t=0}$, $\mu_{100\ t=0}$), $t = 8$ days (measured prior to agitation, $\mu_{10\ t=8\ \mathrm{AVAG}}$, $\mu_{100\ t=8\ \mathrm{AVAG}}$, as well as after agitation, $\mu_{10\ t=8\ \mathrm{APAG}}$, $\mu_{100\ t=8\ \mathrm{APAG}}$) using spindle number 3.

Test n° 1

This test represents the prior art and implements:

- as coupling agent: 0.5 % by dry weight of Poligen™ WE 4, referred to hereafter as coupling agent n°1 (AG1),
- as dispersant:
    - 0.6 % by dry weight of a copolymer consisting of (by weight) 13 % acrylic acid, 15 % butyl acrylate, 31 % methacrylic acid and 40 % styrene, referenced AD1,
    - 0.1 % by dry weight of a copolymer consisting of (by weight) 45 % maleic anhydride and 55 % acrylic acid, referenced AD2.

Test n° 2

This test represents the prior art and implements:

- as coupling agent: 0.5 % by dry weight of Poligen™ WE 4, referenced AG1, and 0.2 % by dry weight of a homopolymer of acrylic acid having a molecular weight of 5 500 g/mol and wherein 70 mole % of the acid groups are neutralised by sodium ions and 30 mole % are neutralised by magnesium ions, referenced AG2,
- as dispersant: 0.6 % by dry weight of AD1, and 0.1 % by dry weight of AD2.

The TOC value was equal to 1 217 ppm, an overly high value. For this reason, no further tests were run using the obtained material from this trial.

Test n° 3

This test represents a comparative example and implements:

- as coupling agent: 0.5 % by dry weight of an acrylic acid homopolymer having a molecular weight of 11 000 g/mol, referred to hereafter as coupling agent n° 2 and referenced AG3

The TOC value was overly high (greater than 12 000 ppm). Therefore, no further steps to concentrate and disperse the resulting product were implemented.

Test n° 4

This test represents a comparative example and implements:

- as coupling agent: 0.5 % by dry weight of copolymer AD1 (also referenced AG4).

The TOC value was equal to 688 ppm, an overly high value.

Test n° 5

This test represents a comparative example and implements:

- as coupling agent: 0.5 % by dry weight of a copolymer consisting of (by weight) 14 % acrylic acid, 5 % methacrylic acid and 81 % polyethylene glycol methoxy methacrylate having a molecular weight of 2 000 g/mol, referred to hereafter as coupling agent n° 5 and referenced AG5,

- and as dispersant: 0.6 % by dry weight of copolymer AD1, and 0.1 % by dry weight of copolymer AD2.

The TOC value was overly high (451 ppm), though lower than that obtained in Tests 2, 3 and 4.

Test n° 6

This test represents a comparative example and implements:

- as coupling agent: 0.5 % by dry weight of a hydrosoluble copolymer consisting of (by weight) 85 % acrylic acid and 15.0 % by weight of a monomer of Formula (I) in which R represents a methacrylic ester, R' represents a linear alkyl chain having 8 carbon atoms, $m = p = 0$, $q = 1$, $n = 25$, referred to hereafter as coupling agent n° 6, referenced AG6,
- and as dispersant: 0.6 % by dry weight of copolymer AD1 and 0.1 % by dry weight of copolymer AD2.

The TOC was around 300 ppm, which remains high though not as high as measured in the previous tests. Overly high viscosity values were encountered on dispersing the filter cake (see Table 1).

Test n° 7

This test represents the invention and implements:

- as coupling agent: 0.5 % by dry weight of a hydrosoluble copolymer consisting of (by weight) 60.0 % acrylic acid, 1.0 % methacrylic acid, 15 % ethyl acrylate and 24.0 % by weight of a monomer of Formula (I) in which R represents a methacrylic ester, R' represents 2-hexyl-1-decanyl, $m = p = 0$, $q = 1$, $n = 25$, referred to hereafter as coupling agent n° 7 and referenced AG7,
- and as dispersant: 0.6 % by dry weight of copolymer AD1 and 0.1 % by dry weight of copolymer AD2.

Test n° 8

This test represents the invention and implements:

- as coupling agent: 0.5 % by dry weight of a hydrosoluble copolymer consisting of (by weight) 85.0 % acrylic acid, and 15.0 % by weight of a monomer of

Formula (I) in which R represents a methacrylic ester, R' represents 2-hexyl-1-dodecanyl, m = p = 0, q = 1, n = 25, referred to hereafter as coupling agent n° 8 and referenced AG8,

- and as dispersant: 0.6 % by dry weight of copolymer AD1 and 0.1 % by dry weight of copolymer AD2.

Test n° 9

This test represents the invention and implements:

- as coupling agent: 0.5 % by dry weight of a hydrosoluble copolymer consisting of (by weight) 85.0 % acrylic acid, and 15.0 % by weight of a monomer of Formula (I) in which R represents a methacrylic ester, R' represents a linear alkyl chain having 22 carbon atoms, m = p = 0, q = 1, n = 25, referred to hereafter as coupling agent n° 9 and referenced AG9,
- and as dispersant: 0.6 % by dry weight of copolymer AD1 and 0.1 % by dry weight of copolymer AD2.

Test n° 10

This test represents the invention and implements:

- as coupling agent: 0.5 % by dry weight of a hydrosoluble copolymer consisting of (by weight) 85.0 % acrylic acid, and 15.0 % by weight of a monomer of Formula (I) in which R represents a methacrylic ester, R' represents a branched alkyl chain having 32 carbon atoms, m = p = 0, q = 1, n = 25, referred to hereafter as coupling agent n° 10 and referenced AG10,
- and as dispersant: 0.6 % by dry weight of copolymer AD1 and 0.1 % by dry weight of copolymer AD2.

Test n° 11

This test represents the invention and implements:

- as coupling agent: 0.5 % by dry weight of a hydrosoluble copolymer consisting of (by weight) 85.0 % acrylic acid, and 15.0 % by weight of a monomer of Formula (I) in which R represents a nonylphenol, m = p = 0, q = 1, n = 25, referred to hereafter as coupling agent n° 11 and referenced AG11,
- and as dispersant: 0.6 % by dry weight of copolymer AD1 and 0.1 % by dry weight of copolymer AD2.

Test n° 12

This test represents the invention and implements:

- as coupling agent: 0.5 % by dry weight of a hydrosoluble copolymer consisting of (by weight) 85.0 % acrylic acid, and 15.0 % by weight of a monomer of Formula (I) in which R represents a linear alkyl chain having 12 carbon atoms, $m = p = 0$, $q = 1$, $n = 23$, referred to hereafter as coupling agent n° 12 and referenced AG12,
- and as dispersant: 0.6 % by dry weight of copolymer AD1 and 0.1 % by dry weight of copolymer AD2.

Table 1

Test n°		1	2	3	4	5	6
Invention (IN) Prior Art (PA) Comparison (CO)		PA	PA	CO	CO	CO	CO
Coupling agent	nature	AG1	AG1-AG2	AG3	AG4 (=AD1)	AG5	AG6
	dose (%)	0.5	0.5-0.2	0.5	0.5	0.5	0.5
% < 2 µm		96	97.7	96.1	96	95.3	
% < 1 µm		76.3	73	74.6	73.5	73.9	
TOC (ppm)		142	1217	12672	688	451	305
Dispersing agent	nature	AD1-AD2	-	-	-	- -	AD1-AD2
	dose (%)	0.6-0.1	-	-	-	- -	0.6-0.1
Solids (%)		48.9	-	-	-	- -	48.8
µ10 *t*=0		630	-	-	-	- -	3500
µ100 *t*=0		190	-	-	-	- -	720
µ10 *t*=8 AVAG		1960	-	-	-	- -	7350
µ100 *t*=8 AVAG		530	-	-	-	- -	2520
µ10 *t*=8 APAG		840	-	-	-	- -	8950
µ100 *t*=8 APAG		220	-	-	-	- -	1200

Table 1 (continued)

Test n°		7	8	9	10	11	12
Invention (IN) Prior Art (PA) Comparison (CO)		IN	IN	IN	IN	IN	IN
Coupling agent	nature	AG7	AG8	AG9	AG10	AG11	AG12
	dose (%)	0.5	0.5	0.5	0.5	0.5	0.5
% < 2 µm		97.1	96,2	97.4	97.1	96.8	97.3
% < 1 µm		76.3	76.5	75.8	74.6	73.8	73.6
TOC (ppm)		140	98	70	116	124	111
Dispersing agent	nature	AD1-AD2	AD1-AD2	AD1-AD2	AD1-AD2	AD1-AD2	AD1-AD2
	dose (%)	0.6-0.1	0.6-0.1	0.6-0.1	0.6-0.1	0.6-0.1	0.6-0.1
Solids (%)		47.3	50.5	50.5	50.3	52.6	48.6
µ10 *t*=0		410	950	700	820	1200	600
µ100 *t*=0		410	235	170	200	280	150
µ10 *t*=8 AVAG		4220	1240	530	970	1180	1290
µ100 *t*=8 AVAG		650	290	210	220	400	300
µ10 *t*=8 APAG		3450	500	410	400	1310	640
µ100 *t*=8 APAG		450	122	100	100	260	140

The above results demonstrate that only the process of the invention, implementing the selected coupling agents, lead to low TOC values (less than 200 ppm), as well as to time-stable aqueous suspensions of self-binding pigment particles.

Example 2

This example represents a process to prepare an aqueous suspension of self-binding pigment particles involving a step of grinding calcium carbonate, a binder and a coupling agent, as well as a concentration step followed by a dispersing step, unless otherwise indicated.

The same protocol as in Example 1 was implemented, except that the dispersing was performed to reach a solids content of 68 % by dry weight.

<u>Test n° 13</u>

This test represents the invention and implements:

- as coupling agent: 0.5 % by dry weight of copolymer AG7,
- and as dispersant: 0.6 % by dry weight of copolymer AD1 and 0.1 % by dry weight of copolymer AD2,

The obtained results (Table 2) show that the process of the invention, implementing the selected coupling agents lead to low TOC values (less than 200 ppm), as well as to time-stable aqueous suspensions of such pigments.

Table 2

Test n°		13
Coupling agent	nature	AG13(=AG7)
	dose (%)	0.5
% < 2 µm		
% < 1 µm		
TOC (ppm)		141
Dispersing agent	nature	AD1-AD2
	dose (%)	0.5-0.1
Solids (%)		68.8
µ10 *t*=0		10
µ100 *t*=0		39
µ10 *t*=8 AVAG		10
µ100 *t*=8 AVAG		32
µ10 *t*=8 APAG		20
µ100 *t*=8 APAG		50

Example 3

This example represents a process to prepare an aqueous suspension of self-binding pigment particles involving a step of grinding calcium carbonate, a binder and a coupling agent, without any subsequent dispersing step.

The same protocol as in Example 1 is implemented, except that the grinding is performed at a solids content of 70 % by dry weight. In this case, a fraction of the suspension was filtered following grinding and the TOC measurement made on the collected water.

Brookfield viscosity measurements were made directly on the suspension obtained following grinding.

Test n° 14

This test represents the invention and implements as coupling agent 0.5 % by dry weight of copolymer AG7.

The results obtained (Table 3) show that the process according to the present invention, implementing the selected coupling agent, lead to low TOC values (less than 200 ppm), as well as to time-stable aqueous suspensions of such pigments. Moreover, this coupling agent allowed grinding to take place at a high solids content (70 % by dry weight).

Table 3

Test n°		14
Coupling agent	nature	AG14(=AG7)
	dose (%)	0.5
% < 2 µm		97.7
% < 1 µm		70.0
TOC (ppm)		
Solids (%)		70
µ10 *t*=0		1250
µ100 *t*=0		350
µ10 *t*=8 AVAG		1390
µ100 *t*=8 AVAG		520
µ10 *t*=8 APAG		1420
µ100 *t*=8 APAG		610

Example 4

This example represents a process to prepare an aqueous suspension of self-binding pigment particles involving a step of grinding calcium carbonate, a binder and a coupling agent, as well as a concentration step followed by a dispersion step, unless otherwise indicated.

In each of the following tests, the listed coupling agent as well as 9 % by weight of a styrene-acrylate binder (commercialised by BASF™ under the trade name Acronal™ S 728) were added to an aqueous suspension of natural calcium carbonate (Norwegian marble) having a solids content of 20 % by dry weight.

Following grinding, the weight fractions of particles in suspension having a diameter of less than 1 and less than 2 µm (% < 1 µm and % < 2 µm, respectively) were determined using Sedigraph™ 5100 instrumentation commercialised by MICROMERITICS™.

Each suspension was then concentrated by filtration on a Büchner™ filter press to obtain a filter cake.

The obtained filter cakes were subsequently dispersed using the listed dispersing agent(s) in order to obtain a suspension having a solids content of approximately 57 to 65 % by weight.

The Brookfield™ viscosities of the obtained suspensions at 25°C under 10 and 100 rpm were determined at time $t = 0$ ($\mu_{100\ t=0}$) using spindle number 2 if the viscosity was between 80 and 200 mPa.s, and spindle 3 if the viscosity was between 200 and 800 mPa.s.

<u>Test n° 15-18</u>

This test represents the invention and implements:

- as coupling agent: in the amount, in % dry weight, of a hydrosoluble copolymer indicated in the Table herebelow, and consisting of (by weight) 60.0 % acrylic acid, 1.0 % methacrylic acid, 15 % ethyl acrylate and 24.0 % by weight of a monomer of Formula (I) in which R represents a methacrylic ester, R' represents 2-hexyl-1-decanyl, m = p = 0, q = 1, n = 25, referred to hereafter as coupling agent n° 7 and referenced AG7,
- as dispersant:
  - 0.5 % by dry weight of a copolymer consisting of (by weight) 13 % acrylic acid, 15 % butyl acrylate, 31 % methacrylic acid and 40 % styrene, referenced AD1,

- 0.1 % by dry weight of a copolymer consisting of (by weight) 45 % maleic anhydride and 55 % acrylic acid, referenced AD2.

Table 4

Test n°		15	16	17	18
Invention (IN)		IN	IN	IN	IN
Coupling agent	nature	AG7	AG7	AG7	AG7
	dose (%)	0.1	0.2	0.4	1.0
% < 2 µm		96	96	96	96
% < 1 µm		75	75	75	77
Dispersing agent	nature	AD1-AD2	AD1-AD2	AD1-AD2	AD1-AD2
	dose (%)	0.5-0.1	0.5-0.1	0.5-0.1	0.5-0.1
Solids (%)		58	57	62	65
µ100 *t*=0		120	100	140	170

CLAIMS

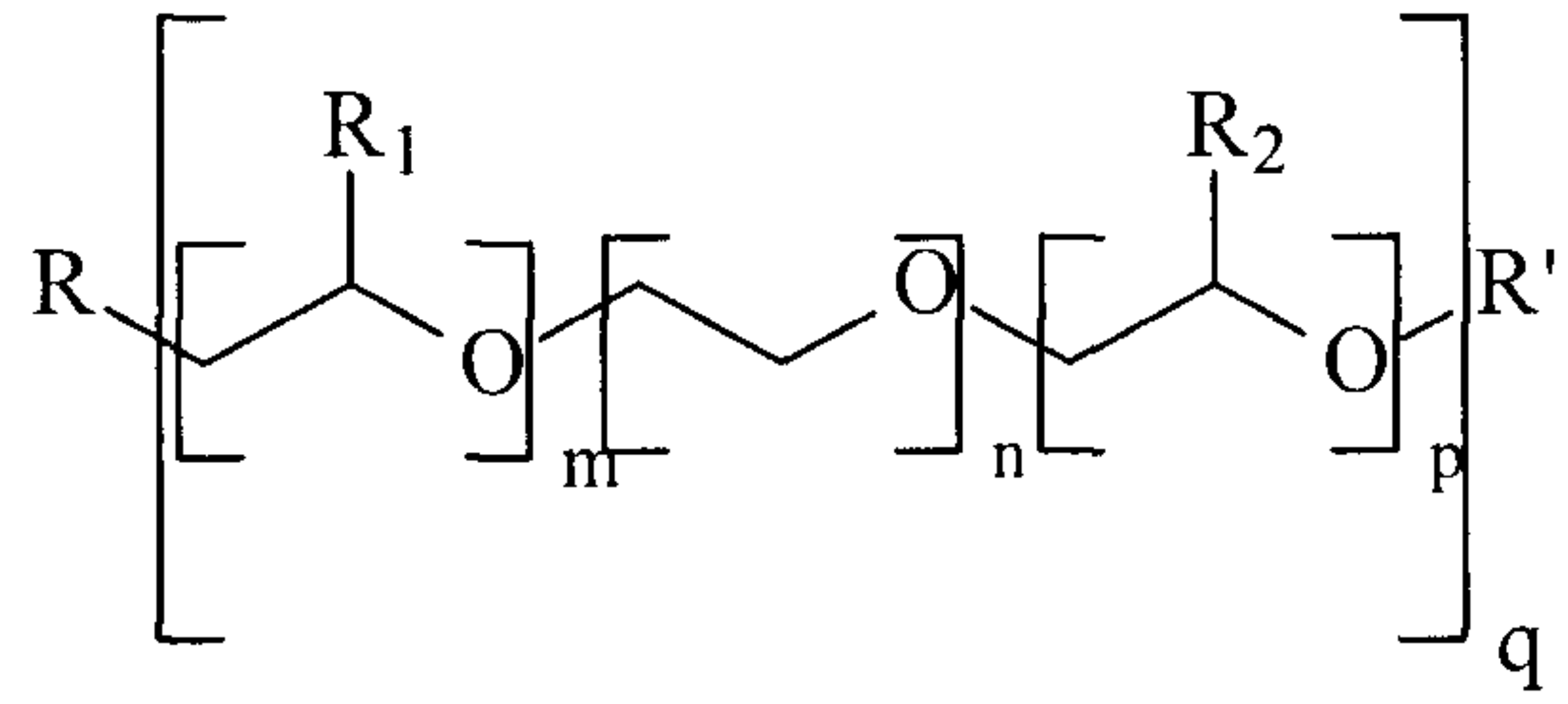
1. Process to prepare self-binding pigment particles comprising the following steps:

a) at least one step of grinding one or more binders and one or more mineral materials in an aqueous environment to obtain a suspension;
b) optionally, at least one step of concentrating the suspension obtained following step a), optionally in the presence of one or more dispersing aids;
c) optionally, drying the suspension obtained following steps a) or b) ;

characterised in that :

- prior to and/or during step a), a copolymer is added in the form of an aqueous solution, said copolymer resulting from the polymerisation of:

2.1) at least one anionic monomer that is an alkene;
2.2) at least one oxyalkylated monomer that is a monomer of Formula (I):



Formula (I)

wherein :

- m, n, p and q are whole numbers having a value of less than 150, and at least one of m, n, and p has a value of greater than 0, q has a value greater than or equal to 1;
- R represents a radical having a polymerisable alkene group,
- R_1 and R_2 are the same or different, and represent hydrogen or alkyl groups,

- R' represents an alkyl, aryl, alkyl aryl or aryl alkyl hydrocarbon chain having 10 to 32 carbon atoms;

2.3) optionally, at least one other monomer that is an acrylic ester.

2. The process according to claim 1, characterised in that in Formula (I), m, n, p and q are whole numbers having a value < 150 and at least one of m, n and p has a value > 0, q has a value $\geq$ to 1 such that $15 \leq (m+n+p)q \leq 150$.

3. The process according to claim 1 or 2, characterised in that in Formula (I), m, n, p and q are whole numbers having a value < 150 and at least one of m, n and p has a value $>$ than 0, q has a value $\geq$ to 1 such that $20 \leq (m+n+p)q \leq 60$.

4. The process according to any one of claims 1 to 3, characterised in that in Formula (I), m, n, p and q are whole numbers having a value < 150 and at least one of m, n and p has a value > 0, q has a value $\geq$ to 1 such that $25 \leq (m+n+p)q \leq 50$.

5. A process according to any one of claims 1 to 4, characterised in that the acrylic ester is ethyl acrylate, an unsaturated amide or mixtures thereof.

6. The process according to claim 5, characterised in that the unsaturated amide is acrylamide.

7. The process according to any one of claims 1 to 6, characterised in that said monomers are present in said copolymer in the following % by weight relative to the total copolymer weight:

2.1) from 5 to 95 % by weight of said anionic monomer(s);
2.2) from 5 to 95 % by weight of said oxyalkylated monomer(s);
2.3) from 0 to 30 % by weight of said other monomer(s).

8. The process according to claim 7, characterised in that the anionic monomer(s) are present in said copolymer from 50 to 95 % by weight relative to total copolymer weight.

9. The process according to claim 7, characterised in that the anionic monomer(s) are present in said copolymer from 70 to 95 % by weight relative to the total copolymer weight.

10. The process according to any one of claims 7 to 9, characterised in that the oxyalkylated monomer(s) are present from 5 to 50 % by weight relative to the total copolymer weight.

11. The process according to any one of claims 7 to 9, characterised in that the oxyalkylated monomer(s) are present from 5 to 30 % by weight relative to the total copolymer weight.

12. The process according to any one of claims 7 to 11, characterised in that said other monomer(s) are present from 0 to 20 % by weight relative to the total copolymer weight.

13. The process according to any one of claims 1 to 12, characterised in that said anionic monomer is acrylic acid, methacrylic acid or mixtures thereof.

14. The process according to any one of claims 1 to 13, characterised in that R' is a branched hydrocarbon chain having 10 to 24 carbon atoms.

15. The process according to claim 14, characterised in that the branched hydrocarbon chain having 10 to 24 carbon atoms results from the condensation of linear alcohols according to the Guerbet reaction.

16. The process according to claim 14 or 15, characterised in that R' is 2-hexyl-1-decanyl, 2-octyl-1-dodecanyl or mixtures thereof.

17. The process according to any one of claims 1 to 13, characterised in that R' is a polystyryl phenol.

18. The process according to claim 17, characterised in that the polystyryl phenol is distyrylphenol, tristyrylphenol or mixtures thereof.

19. The process according to any one of claims 1 to 18, characterised in that the radical R is (a) hydrocarbon radicals, (b) radicals forming oxyalkyl esters, (c) radicals forming N-oxyalkylurethanes, (d) radicals forming oxyalkyl ethers, (e) radicals forming oxyalkyl amides, (f) radicals forming oxyalkyl imides, or (g) mixtures thereof.

20. The process according to claim 19, characterised in that the hydrocarbon radicals are vinyl radicals, allyl radicals or a mixture thereof.

21. The process according to claim 19 or 20, characterised in that the radicals forming oxyalkyl esters are acrylic acid, methacrylic acid, maleic acid or a mixture thereof.

22. The process according to any one of claims 19 to 21, characterised in that the radicals forming N-oxyalkylurethanes are radicals of acrylurethane, methacrylurethane, α-α' dimethyl-isopropenyl-benzylurethane, allylurethane or mixtures thereof.

23. The process according to claims 19 to 22, characterised in that the radicals forming oxyalkyl ethers are radicals forming vinyl oxyalkyl ethers, radicals forming allyl oxyalkyl ethers, radicals forming oxyalkylurethanes or mixtures thereof.

24. The process according to claim 19, characterised in that R is a radical forming an oxyalkyl methacrylic ester.

25. The process according to any one of claims 1 to 24, characterised in that said copolymer features a molar % of neutralisation of any acidic functional groups by one or more neutralising agent(s) of from 0 to 50 %.

26. The process according to any one of claims 1 to 24, characterised in that said copolymer features a molar % of neutralisation of any acidic functional groups by one or more neutralising agent(s) of from 0 to 35 %.

27. The process according to any one of claims 1 to 24, characterised in that said copolymer features a molar % of neutralisation of any acidic functional groups by one or more neutralising agent(s) of from 0 to 20 %.

28. The process according to any one of claims 25 to 27, characterised in that said neutralisation agent is hydroxides of sodium, potassium, lithium or mixtures thereof.

29. The process according to any one of claims 1 to 28, characterised in that said one or more dispersing aid in step b) is an acrylic acid homo or copolymer.

30. The process according to any one of claims 1 to 29, characterised in that the solids content of the suspension ground during step a) is from 1 to 80 % by dry weight relative to the total weight of said suspension.

31. The process according to any one of claims 1 to 29, characterised in that the solids content of the suspension ground during step a) is from 15 to 60 % by dry weight relative to the total weight of said suspension.

32. The process according to any one of claims 1 to 31, characterised in that said mineral material is metal oxides, metal hydroxides, carbonates, gypsum, satin white or mixtures thereof.

33. The process according to claim 32, characterised in that the metal oxides are titanium dioxide, aluminium trioxide or mixtures thereof.

34. The process according to claim 32 or 33, characterised in that the metal hydroxides are aluminium trihydroxide, sulphites or silicates.

35. The method of claim 34, characterised in that the silicates are talc, kaolin clay, mica or mixtures thereof.

36. The process according to any one of claims 32 to 35, characterised in that the carbonates are calcium carbonate, dolomite or mixtures thereof.

37. The process according to any one of claims 1 to 36, characterised in that said binder is (a) binders of natural origin or (b) synthetic binders or (c) mixtures thereof.

38. The process according to claim 37, characterised in that the binders of natural origin are starch, proteins, cellulose or cellulosic derivatives.

39. The process according to claim 38, characterised in that the proteins are casein.

40. The process according to claim 38, characterised in that the cellulosic derivatives are ethylhydroxyethyl cellulose (EHEC), carboxymethylcellulose (CMC) or mixtures thereof.

41. The process according to any one of claims 37 to 40, characterised in that the synthetic binders are polyvinyl acetate (PVA) or acrylic binders.

42. The process according to claim 41, characterised in that the acrylic binders are acrylic ester binders, acrylonitrile binders, styrene-acrylic binders, styrene binders, styrene-butadiene binders, butadiene binders or mixtures thereof.

43. The process according to any one of claims 1 to 42, characterised in that during step a) the weight proportion of mineral material:binder contained in the suspension is between 99:1 and 1:99.

44. The process according to any one of claims 1 to 42, characterised in that during step a) the weight proportion of mineral material:binder contained in the suspension is between 70:30 and 30:70.

45. The process according to any one of claims 1 to 44, characterised in that said copolymer is implemented in an amount corresponding to 0.1 to 2 % by dry weight relative to the dry weight of mineral material.

46. The process according to any one of claims 1 to 44, characterised in that said copolymer is implemented in an amount corresponding to 0.1 to 0.5 % by dry weight relative to the dry weight of mineral material.

47. The process according to any one of claims 1 to 44, characterised in that said copolymer is implemented in an amount corresponding to 0.1 to 0.3 % by dry weight relative to the dry weight of mineral material.

48. The process according to any one of claims 1 to 47, characterised in that during any step b) from 0.01 to 2 % by weight, relative to the dry weight of mineral material, of at least one dispersing agent is added.