

ORGANIC POLYMER-CALCIUM CARBONATE COMPOSITE
PARTICLES, HOLLOW CALCIUM CARBONATE PARTICLES,
PROCESSES FOR THEIR PREPARATION, THEIR USE AS
FILLERS OR ADDITIVES IN PLASTICS AND
ELASTOMERS

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The present invention relates to composite particles based on an organic polymer and calcium carbonate, to hollow calcium carbonate particles and to suspensions of these particles. It also relates to processes for the preparation
10 of these particles and of these suspensions and to their use as fillers or additives in plastics and elastomers.

Calcium carbonate is known to impart good rigidity to thermoplastic materials by the introduction of particles based on calcium carbonate of the order of a micron into the
15 plastic. The latter then exhibits improved behaviour.

However, it has been found that plastics reinforced with calcium carbonate become much more brittle and that their impact strength is weakened.

Furthermore, it is known to introduce inorganic
20 fillers in the form of particles of silica or of carbon black into elastomers, and in particular into elastomers for tyres, in order to improve the tear and abrasion resistance of the elastomers. In turn, however, these reinforced tyres lack flexibility at low temperature.

25 The present invention seeks to provide a product allowing the impact strength and rigidity properties of plastics to be reinforced at the same time and a process enabling said product to be manufactured.

The present invention also seeks to provide a
30 product which makes it possible to impart low-temperature flexibility to elastomers and a process enabling said product to be manufactured.

The present invention therefore provides composite particles having a mean diameter not exceeding 5 μm and
35 comprising an organic polymer core at least partly covered with calcium carbonate.

The present invention further provides hollow

particles having a mean diameter not exceeding 5 μm and consisting of a calcium carbonate shell.

The present invention also provides suspensions of the above composite particles and suspensions of the above
5 hollow particles.

The present invention additionally provides a process for the preparation of a suspension of the above composite particles which comprises contacting a latex with calcium dihydroxide and then adding carbon dioxide to the
10 mixture to cause precipitation of the calcium carbonate on the latex particles.

The invention additionally provides a process for the preparation of the composite particles wherein the suspension obtained by the above process is dried.

15 The invention also provides processes for the preparation of the hollow particles. According to a first method the composite particles defined above are calcined. According to a second method these same composite particles are placed in a solvent for the organic polymer to dissolve
20 the organic polymer core, the mixture is centrifuged and the hollow particles obtained are dried.

The invention furthermore provides the use of the composite particles as fillers or additives in plastics and elastomers and the use of the hollow particles as fillers in
25 elastomers.

The composite particles according to the invention are particles of organic polymer, the surface of which is at least partly covered with a precipitate of calcium carbonate. The calcium carbonate may cover each organic polymer core
30 merely partly or completely. It is also possible for the calcium carbonate to be partly embedded in the outer peripheral layer of the organic polymer core.

These composite particles are generally spherical in shape.

35 The calcium carbonate is usually in calcite form.

The nature of the organic polymers forming part of the composition of the composite particles is of the type of latex particles, that is to say particles of (co)polymers originating from conventional processes for emulsion

(co)polymerization of copolymerizable organic monomers.

Among these (co)polymers forming part of the composition of the composite particles there may be mentioned especially those originating from the polymerization of the following monomers:

a): alkyl, hydroxyalkyl and chloroalkyl (meth)acrylates and alkyl or hydroxyalkyl chloroacrylates in which the alkyl radical preferably contains from 1 to 18 carbon atoms, such as:

- 10 - methyl (meth)acrylate,
- ethyl or hydroxyethyl (meth)acrylate,
- propyl or hydroxypropyl (meth)acrylate,
- n-butyl, isobutyl or hydroxybutyl
 meth)acrylate,
- 15 - amyl, lauryl and/or isoamyl (meth)acrylate,
- 2-ethylhexyl, ethyl, octyl, methyl, butyl,
 3,3'-dimethylbutyl, isobutyl and/or isopropyl
 (meth)acrylate,
- chloroethyl (meth)acrylate, and
- 20 - butyl, methyl, ethyl, isopropyl and/or
 cyclohexyl chloroacrylate;

b): vinyl or allyl esters of linear or branched C_1 - C_{12} saturated carboxylic acids, such as:

- vinyl acetate,
- 25 - vinyl propionate,
- vinyl butyrate,
- allyl acetate,
- vinyl versatate® (registered trademark for
 esters of C_9 - C_{11} α -branched acids),
- 30 - vinyl laurate,
- vinyl benzoate,
- vinyl trimethylacetate,
- vinyl pivalate, and
- vinyl trichloroacetate;

35 c): esters and half-esters of α,β -ethylenically unsaturated polycarboxylic acids containing from 4 to 24 carbon atoms, such as:

- methyl, dimethyl, ethyl, butyl and/or
 2-ethylhexyl fumarate, and

- methyl, dimethyl, ethyl, butyl and/or 2-ethylhexyl maleate;
 - d): vinyl halides such as:
 - vinyl and/or vinylidene chloride and/or fluoride;
 - e): fluoroolefins such as tetrafluoroethylene;
 - f): vinylaromatics preferably containing not more than 24 carbon atoms and chosen in particular from:
 - styrene,
 - α -methylstyrene, 4-methylstyrene, 2-methylstyrene, 3-methylstyrene,
 - 4-methoxystyrene,
 - 2-hydroxymethylstyrene,
 - 4-ethylstyrene,
 - 4-ethoxystyrene,
 - 3,4-dimethylstyrene,
 - 2-chlorostyrene, 3-chlorostyrene,
 - 4-chloro-3-methylstyrene,
 - 4-tert-butylstyrene,
 - 4-dichlorostyrene, 2,6-dichlorostyrene, 2,5-difluorostyrene,
 - 1-vinylnaphthalene, and
 - vinyltoluene;
 - g): conjugated aliphatic dienes preferably containing from 3 to 12 carbon atoms, such as
 - 1,3-butadiene,
 - isoprene, and
 - 2-chloro-1,3-butadiene; and
 - h): α,β -ethylenically unsaturated nitriles preferably containing from 3 to 6 carbon atoms, such as acrylonitrile and methacrylonitrile.
- Some of these main monomers can be copolymerized with up to 10% by weight of other monomers, so-called comonomers, of ionic nature, such as:
- the α,β -ethylenically unsaturated carboxylic acid monomers mentioned above, including mono- and polycarboxylic acids such as:
 - acrylic acid,
 - methacrylic acid,

maleic acid,
itaconic acid,
fumaric acid, and
crotonic acid;

5 - ethylenic monomers containing secondary, tertiary
or quaterized amine groups, such as: vinylpyridines,
diethylaminoethyl methacrylate;

 - sulphonated ethylenic monomers such as: vinyl
sulphonate, styrene sulphonate;

10 - zwitterionic ethylenic monomers such as
sulphopropyl-(dimethylaminopropyl) acrylate;

 - amides of unsaturated carboxylic acids, such as:
acrylamide, methacrylamide; and

 - esters of (meth)acrylates and of polyhydroxypropyl
15 or polyhydroxyethylated alcohols.

 Anionic polymers, such as polyvinyl acetate, or
amphoteric polymers can also be employed within the scope of
the present invention.

 Copolymers of styrene with acrylates may be
20 mentioned more particularly. They may advantageously be
chosen from butadiene-styrene copolymers containing
carboxylate, sulphate or sulphonate functional groups, and
butadiene-styrene-acrylamide copolymers.

 In the composite particles according to the
25 invention the organic polymer preferably has a carboxylate
functional group content of from 1 to 50% by weight of
ion-forming monomers present in the organic polymer, and an
amide functional group content of less than 5% by weight of
ion-forming monomers present in the organic polymer.

30 The organic polymers generally have a glass
transition temperature of from -80°C to 200°C.

 The composite particles usually have a dispersion
index of not more than 0.50, and preferably lower than 0.30.

 The dispersion index is determined, here and in the
35 case of all the other dispersion indices defined in the text,
by the formula:

$$I = \frac{\phi_{84} - \phi_{16}}{2\phi_{50}}$$

in which:

- ϕ_{84} is the particle diameter wherein 84% of the particles have a diameter smaller than ϕ_{84} ,

- ϕ_{16} is the particle diameter wherein 16% of the particles have a diameter smaller than ϕ_{16} ,

- ϕ_{50} is the mean particle diameter.

The dispersion index is measured by transmission electron microscopy (TEM).

The composite particles according to the invention have a mean diameter not exceeding 5 μm . It is usually at least 0.04 μm and preferably from 0.1 to 0.3 μm . The determination of the mean diameter of these particles, and of all the other particles defined in the text, is carried out using TEM.

The diameter of the organic polymer core is usually from 0.04 to 5 μm . The thickness of the shell or of the layer of calcium carbonate generally does not exceed 200 nm. It is usually at least 1 nm, preferably at least 5 nm and more preferably from 5 to 70 nm.

The dimensions given above are given purely by way of guidance, because it may be more or less difficult to determine accurately the size of the organic polymer core and the thickness of the calcium carbonate, insofar as, as indicated above, the latter may be embedded in the outer peripheral layer of the organic polymer core because the organic polymer is soft and deformable. When the organic polymer is soft, for example when it is at a temperature above its glass transition temperature, the calcium carbonate can become embedded therein. The measurements of the size of the organic polymer core and of the thickness of the calcium carbonate will therefore be modified as a result of the existence of an intermediate layer originating from the interaction between the organic polymer and the calcium carbonate.

The composite particles according to the invention preferably have a specific surface of from 1 to 100 m^2/g .

The specific surface is the BET specific surface determined by nitrogen adsorption in accordance with ASTM standard D 3663-78, established from the Brunauer-Emmett-

Teller method described in the periodical "Journal of the American Chemical Society", 60, 309 (1938).

This specific surface may reveal the more or less smooth appearance of the layer of calcium carbonate on the organic polymer.

The invention next relates to hollow particles having a mean diameter not exceeding 5 μm and consisting of a calcium carbonate shell.

The thickness of the calcium carbonate shell generally does not exceed 200 nm. It is usually at least 1 nm, preferably at least 5 nm and more preferably from 5 to 70 nm.

The particles are generally spherical in shape.

The calcium carbonate is preferably in calcite form.

The hollow particles usually have a dispersion index not exceeding 0.50 and preferably lower than 0.30.

The hollow particles have a mean diameter not exceeding 5 μm . It is usually at least 0.04 μm and preferably from 0.1 to 0.3 μm .

The hollow particles preferably have a specific surface of from 1 to 100 m^2/g .

The invention also relates to suspensions including the above composite particles.

In some cases these suspensions will be colloidal dispersions. Throughout the description, a colloidal dispersion means any system consisting of fine particles of colloidal dimensions of organic polymer which are covered with calcium carbonate, in suspension in liquid, especially aqueous, phase. It will be noted that the calcium carbonate may be present either completely in the colloids or simultaneously in the form of ions and in the colloids, without, however, the proportion represented by the ionic form exceeding approximately 10% of the total of the calcium carbonate in the colloidal dispersion. In the invention, colloidal dispersions are preferably used in which the calcium carbonate is completely in the colloids.

As indicated above, it is also possible for the calcium carbonate to be partly embedded in the outer peripheral layer of the organic polymer core.

The composite particles in these suspensions of composite particles have the same characteristics of mean diameter, dispersion index, specific surface and thickness of the shell or of the layer of calcium carbonate as the composite particles defined above.

The liquid phase is an aqueous or optionally hydroalcoholic phase.

The invention also relates to suspensions including the above hollow particles. The liquid phase is generally aqueous or hydroalcoholic.

The hollow particles in these suspensions of hollow particles have the same characteristics of the mean diameter, dispersion index, specific surface and shell thickness as the hollow particles defined above.

A process for the preparation of a suspension of composite particles according to the invention includes the following stages:

- a latex is placed in contact with calcium dihydroxide, and
- carbon dioxide is added to the mixture of latex and of calcium dihydroxide obtained above, whereby calcium carbonate precipitates on the latex particles.

The liquid phase of this starting latex is generally an aqueous phase and preferably water. In the case where the latices have been obtained by dispersion copolymerization of organic monomers the liquid phase may be hydroalcoholic.

The nature of the latex particles is of the type of the polymers of the composite particles defined above.

The calcium dihydroxide is preferably in the form of a suspension of calcium dihydroxide particles of variable size. This calcium dihydroxide suspension may be obtained by various means: from calcium oxide or from a calcium salt to which a base (e.g. NaOH, KOH or NH_3) has been added.

Preference will be given to calcium dihydroxide suspensions in the form of milks of lime. The use of calcium dihydroxide obtained from calcium oxide makes it possible, in fact, to avoid the presence of impurities in the calcium carbonate precipitated at the surface of the latex particles, in contrast to the suspensions originating from, for example,

calcium salts, which introduce ions in solution, such as Cl^- or NO_3^- . It also permits a better control of the dispersion state of the composite particles by reducing the ionic strength to a minimum.

5 The particle concentration of the calcium dihydroxide suspension is advantageously from 0.1 to 3 mol/kg.

 Its viscosity is generally from 0.05 to 0.5 Pa s (viscosity measured at 50 s^{-1}).

10 The implementation of the process consists in mixing the latex and the calcium dihydroxide suspension. This mixing may take place in any order whatever. Carbon dioxide in gaseous form is then introduced into this mixture, whereby calcium carbonate is formed, which precipitates on the latex
15 particles in suspension in the mixture.

 In order to preserve the stability of the latex during the process and to prevent its flocculation, a stabilizer is generally added to the latex before it is placed in contact with the calcium dihydroxide.

20 The stabilizer chosen may be a nonionic surfactant of the type: ethoxylated alkylphenol, polyethylene glycol and/or polyvinylpyrrolidone.

 1 to 50g of stabilizer is generally added per kg of latex, and preferably less than 20g/kg.

25 In the case where a surfactant-type stabilizer is added to the reaction mixture in order to stabilize the latex it may be necessary simultaneously to add a foam-suppressor to avoid the excessive presence of bubbles.

 According to a first alternative form of the
30 process, it is possible to introduce an inhibitor of growth of calcium carbonate into the mixture of latex and of calcium dihydroxide. This inhibitor makes it possible to control the thickness of the layer of calcium carbonate precipitated at the surface of the latex particles.

35 It may be chosen from citric acid, citrates and/or phosphate-based agents and from the latex stabilizers defined above.

 The inhibitor is introduced into the reaction mixture before the carbon dioxide.

The process according to the invention is advantageously carried out at a temperature of from 20 to 40°C. The choice of the temperature makes it possible to vary the final specific surface of the calcium carbonate layer of the particles, insofar as the higher the temperature, the larger will be the size of the precipitated calcium carbonate particles deposited at the surface of the latex particles.

During the process according to the invention carbon dioxide is preferably introduced in the form of a gaseous carbon dioxide/air or nitrogen mixture in a proportion of from 5 to 50% by volume, preferably of the order of 30%. The addition of carbon dioxide is generally made by allowing the gas mixture to bubble through the mixture of latex and of calcium dihydroxide.

The carbon dioxide is usually introduced into the mixture of latex and calcium dihydroxide at a flow rate of from 40 ml/h/kg to 200 l/h/kg of the mixture of latex and of calcium dihydroxide. The flow rate may change as a function of the quantity of latex to be treated and the thickness of the calcium carbonate layer which it is intended to precipitate on the latex particles.

According to a second alternative form of the process, the latter may include an additional stage of maturing after the precipitation of calcium carbonate on the latex particles. Its objective is to create a more spherical layer of calcium carbonate on the latex particles and to decrease the specific surface of this calcium carbonate layer at the surface of the latex particles. This stage of maturing is performed by heating the reaction mixture or simply by leaving it undisturbed at the reaction temperature.

The invention also relates to a process for the preparation of organic polymer - calcium carbonate composite particles, wherein the suspensions obtained by the process described above or one of its alternative forms are dried.

According to a preferred embodiment of the invention the separation of the composite particles from the reaction mixture and their drying are carried out by atomization, that is to say by spraying the mixture into a hot atmosphere (spray-drying). The atomization may be carried out by means

of any sprayer known per se, for example using a spray nozzle of the watering rose or other type. So-called turbine atomizers may also be employed. For the various spraying techniques capable of being used in the present process, reference may be made especially to the fundamental work by Masters, entitled "Spray-drying" (second edition, 1976, George Godwin Publishers - London).

It will be noted that it is also possible to carry out the spray-drying operation by means of a "flash" reactor, for example of the type developed by the Applicant Company and described especially in FR-A-2,257,326, FR-A-2,419,754 and FR-A-2,431,321. In this case the process gases (hot gases) are propelled with a helical motion and flow into a vortex well. The mixture to be dried is injected along a trajectory coinciding with the axis of symmetry of the helical trajectories of the said gases, and this allows the quantity of motion of the gases to be transferred completely to the mixture to be treated. The gases thus perform, in fact, a dual function: on the one hand the comminution, that is to say the conversion of the initial mixture into fine droplets and, on the other hand, the drying of the droplets obtained. Furthermore, the extremely short residence time (generally shorter than approximately 1/10 of a second) of the particles in the reactor has the advantage, among others, of limiting possible risks of overheating as a result of an excessively long contact with the hot gases.

Depending on the respective flow rates of the gases and of the mixture to be dried, the entry temperature of the gases is from 400 to 900°C and more particularly from 600 to 800°C, and the temperature of the dried solid is from 150 to 300°C.

With regard to the flash reactor referred to above, reference may be made especially to Figure 1 of FR-A-2,431,321.

This consists of a combustion chamber and of a contact chamber made up of a venturi or of a truncated cone whose upper part diverges. The combustion chamber opens into the contact chamber via a small passage.

The upper part of the combustion chamber is provided

with an opening permitting the introduction of the combustible phase.

Furthermore, the combustion chamber includes a coaxial internal cylinder, thus defining inside it a central region and an annular peripheral region, which has perforations, most of which are situated towards the upper part of the apparatus. The chamber includes at least six perforations distributed over at least one circle, but preferably over a number of axially spaced circles. The total area of the perforations located in the lower part of the chamber may be very small, of the order of 1/10 to 1/100 of the total area of the perforations of the said coaxial internal cylinder.

The perforations are usually circular and have a very small thickness. The ratio of their diameter to the wall thickness is preferably at least 5:1, the minimum thickness of the wall being limited only by mechanical essentials.

Finally, a pipe elbow emerges into the small passage, the end of which opens into the axis of the central region.

The gaseous phase driven with a helical motion (called helical phase in what follows) is composed of a gas, generally air, introduced into an orifice made in the annular region; this orifice is preferably situated in the lower part of the said region.

In order to obtain a helical phase at the small passage, the gaseous phase is preferably introduced at low pressure into the abovementioned orifice, that is to say at a pressure which is lower than 1 bar and more particularly at a pressure which is from 0.2 to 0.5 bar above the pressure existing in the contact chamber. The velocity of this helical phase is generally from 10 to 100 m/s and preferably from 30 to 60 m/s.

Moreover, a combustible phase, which may be methane in particular, is injected axially through the abovementioned opening into the central region at a velocity of approximately 100 to 150 m/s.

The combustible phase is ignited by any known means in the region where the fuel and the helical phase are in

contact.

Next, the forced flow of the gases in the small passage takes place along a set of trajectories coinciding with groups of generatrices of a hyperboloid. These
5 generatrices are based on a group of circles, of small-sized rings located near and below the small passage, before diverging in all directions.

The mixture to be treated is next introduced in the form of liquid through the abovementioned pipe. The liquid is
10 then broken up into a multitude of drops, each of them being carried by a volume of gas and subjected to a motion creating a centrifugal effect. The flow rate of the liquid is usually from 0.03 to 10 m/s.

The ratio of the quantity of proper motion of the
15 helical phase to that of the liquid mixture must be high. In particular it is at least 100:1 and preferably from 1000:1 to 10000:1. The quantities of motion at the small passage are calculated as a function of the entry flow rates of the gas and of the mixture to be treated and of the section of the
20 said passage. An increase in the flow rates produces an increase in the size of the drops.

In these conditions the proper motion of the gases is imposed in its direction and its intensity on the drops of the mixture to be treated, which are separated from one
25 another in the region of convergence of the two streams. The velocity of the liquid mixture is additionally reduced to the minimum needed to obtain a continuous flow.

According to another preferred method the atomization is carried out in such a way that the temperature
30 of entry into the atomizer is of the order of 200°C and that at the exit is of the order of 120°C.

The composite particles in suspension may be optionally subjected to a treatment imparting water-repellency before the atomization operation, in order to
35 prevent their agglomeration during this atomization stage. This treatment imparting water-repellency is found to be more or less necessary, depending on the chemical nature of the agent for treatment imparting water-repellency and on that of the suspension medium.

The invention additionally relates to the process for the preparation of the hollow calcium carbonate particles defined above wherein, according to a first embodiment, the composite particles made up of an organic polymer core
5 covered with calcium carbonate are calcined. The calcination is carried out at a temperature which is sufficient for the organic polymer core of the composite particles to be decomposed into gases. This temperature is usually from 400 to 700°C and is more particularly 650°C. Through this
10 calcination, the organic polymer core is entirely decomposed into gases, which are emitted through the calcium carbonate shell, creating a hollow particle.

According to a preferred alternative form of the first embodiment, the composite particles are subjected to a
15 temperature rise of the order of 3°C/min until the temperature of 650°C is reached. The particles are then kept at this temperature for 5 hours.

According to a second embodiment of the process for the preparation of the hollow calcium carbonate particles the
20 composite particles made up of an organic polymer core covered with calcium carbonate are placed in a solvent for the organic polymer, whereby the organic polymer core is dissolved, the mixture is centrifuged and the hollow particles obtained are dried. The drying is performed at a
25 temperature of from 25 to 200°C.

The invention also relates to the use of the composite particles as fillers or additives in plastics and elastomers.

These products are employed in particular for any
30 plastics intended to be reinforced against impacts, such as polyolefins, polyvinyl chlorides and their derivatives (e.g. polyamides and polystyrenes).

It is found that the introduction of composite particles according to the invention gives the plastics a
35 good rigidity and, at the same time, a higher impact strength.

These particles are also employed in elastomers such as natural rubber, polyisoprene, polybutadiene and copolymers of butadiene and of styrene.

It is found that the introduction of composite particles according to the invention imparts low-temperature flexibility to the elastomers.

The invention relates to the use of the hollow particles as fillers in elastomers. These particles are preferably employed in the same elastomers as those defined above.

It is found that elastomers and in particular tyres acquire a greater low-temperature flexibility as a result of the introduction of hollow particles according to the invention into the matrix.

Examples will now be given.

EXAMPLE 1

The latex employed is of the SB112 type marketed by Rhône-Poulenc; it is a styrene/butadiene/ acrylamide anionic terpolymer of $T_g \approx 0^\circ\text{C}$.

The stabilizer employed for this latex is the surfactant Cemulsol NP30, which is ethoxylated nonylphenol.

Operating conditions:

$T = 25^\circ\text{C}$

Reactants	Reactant mass or flow rate	Characteristics
SB112 latex in suspension in water with a solids content of 30.25%	74.10g	mean diameter = 135 nm
milk of lime containing 2.76 mol/kg of $\text{Ca}(\text{OH})_2$	18.28g	viscosity = 0.05 Pa s
purified water	904.51g	
Cemulsol NP30	3.11g	
CO_2 in the form of CO_2 /air mixture containing 30% of CO_2	40 ml/h/kg	

SB112 latex is introduced into a reactor and then a mixture prepared beforehand, containing the Cemulsol NP30 and the purified water, is added with stirring. The milk of lime is then poured into the reaction mixture and carbon dioxide
5 is bubbled in. Stirring is continued throughout the reaction.

The resistivity of the mixture is measured in parallel. When it becomes higher than 0.5 k Ω the bubbling of CO₂ is stopped.

A suspension of composite particles including an
10 organic polymer core covered with calcium carbonate which are completely individualized, with a diameter of 140 nm, measured by TEM, is obtained.

The dispersion index is 0.4.

The concentration of the suspension is 2.7% by
15 weight.

EXAMPLE 2

Preparation of a dispersion according to the invention

The reactants employed are the same ones as in
Example 1.

20 On the other hand, a foam-suppressor is added in this case, in the form of Rhodorsyl® marketed by Rhône-Poulenc, because of the formation of foams.

	Reactants	Reactant mass or flow rate	Characteristics
5	SB112 latex with a solids content of 60%	212.5g	mean diameter = 135 nm
	Cemulsol NP30	17.7g	
	Rhodorsyl: emulsion with a solids content of 10%	30g	
	purified water	212.5g	
10	milk of lime containing 3.096 mol/kg of Ca(OH) ₂	590g	viscosity = 0.05 Pa s
15	CO ₂ in the form of CO ₂ /N ₂ mixture containing 10% of CO ₂	220 l/h/kg	

SB112 latex is introduced into a reactor and then a mixture prepared beforehand, containing the Cemulsol, the purified water and the Rhodorsyl, is added with stirring. The milk of lime is then poured into the reaction mixture and carbon dioxide is bubbled in. Stirring is continued throughout the reaction.

The resistivity of the mixture is measured in parallel. When it becomes higher than 0.500 kΩ, which corresponds to a reaction for 5 h, the bubbling of CO₂ is stopped.

A suspension of composite particles including an organic polymer core covered with calcium carbonate, which are completely individualized, with a diameter of 160 nm, measured by TEM, is obtained.

The composite particle concentration of the suspension is 30% by weight.

The inorganic carbon content of the suspension of

composite particles is 15.8g/l, that is a CaCO_3 concentration of 132.5g/l.

EXAMPLE 3

Preparation of a suspension according to the invention:

5 The reactants employed are the same ones as in Example 1.

Operating conditions:

$$T = 25^\circ\text{C}$$

	Reactants	Reactant mass or flow rate	Characteristics
10	SB112 latex in suspension containing 30.25%	71.4g	mean diameter = 135 nm
15	milk of lime containing 2.80 mol of $\text{Ca}(\text{OH})_2/\text{kg}$	47.5g	viscosity = 0.05 Pa s
	purified water	927.76g	
	Cemulsol NP30	3.14g	
20	CO_2 in the form of CO_2/N_2 mixture containing 30% of CO_2	220 l/h/kg	

SB112 latex is introduced into a reactor and then a mixture prepared beforehand, containing the Cemulsol and the purified water, is added with stirring. The milk of lime is then poured into the reaction mixture and carbon dioxide is
25 bubbled in. Stirring is continued throughout the reaction.

The resistivity of the mixture is measured in parallel. When it becomes higher than 0.500 k Ω the bubbling of CO_2 is stopped.

A suspension of composite particles including an
30 organic polymer core covered with calcium carbonate which are completely individualized, with a diameter of 145 nm, measured by TEM, is obtained. The theoretical thickness of the calcium carbonate layer is 5 nm.

The concentration of the suspension is 3.2% by

weight.

EXAMPLE 4

Preparation of a suspension according to the invention:

The reactants employed are the same ones as in
5 Example 1.

Operating conditions:

T = 25°C

	Reactants	Reactant mass or flow rate	Characteristics
10	SB112 latex in suspension containing 29.57%	75.89g	mean diameter = 135 nm
	milk of lime containing 2.80 mol of Ca(OH) ₂ /kg	56.42g	viscosity = 0.05 Pa s
15	purified water	918.02g	
	Cemulsol NP30	3.16g	
	CO ₂ in the form of CO ₂ /N ₂ mixture containing 30% of CO ₂	220 l/h/kg	

20 SB112 latex is introduced into a reactor and then a
mixture prepared beforehand, containing the Cemulsol and the
purified water, is added with stirring. The milk of lime is
then poured into the reaction mixture and carbon dioxide is
bubbled in. Stirring is continued throughout the reaction.

25 The resistivity of the mixture is measured in
parallel. When it becomes higher than 0.5 kΩ the bubbling of
CO₂ is stopped.

A suspension of composite particles including an
organic polymer core covered with calcium carbonate which are
30 completely individualized, with a diameter of 155 nm,
measured by TEM, is obtained. The theoretical thickness of
the calcium carbonate layer is 10 nm.

The composite particle concentration of the
suspension is 3.6% by weight.

EXAMPLE 5

Preparation of a suspension according to the invention:

The reactants employed are the same ones as in Example 1.

5 **Operating conditions:**

T = 25°C

	Reactants	Reactant mass or flow rate	Characteristics
10	SB112 latex in suspension containing 30.25%	74.04g	mean diameter = 135 nm
	milk of lime containing 2.80 mol of Ca(OH) ₂ /kg	113.21g	viscosity = 0.05 Pa s
	purified water	861.23g	
15	Cemulsol NP30	3.16g	
	CO ₂ in the form of CO ₂ /N ₂ mixture containing 30% of CO ₂	220 l/h/kg	

SB112 latex is introduced into a reactor and then a
20 mixture prepared beforehand, containing the Cemulsol and the
purified water, is added with stirring. The milk of lime is
then poured into the reaction mixture and carbon dioxide is
bubbled in. Stirring is continued throughout the reaction.

The resistivity of the mixture is measured in
25 parallel. When it becomes higher than 0.5 kΩ the bubbling of
CO₂ is stopped.

A suspension of composite particles including an
organic polymer core covered with calcium carbonate which are
completely individualized, with a diameter of 170 nm,
30 measured by TEM, is obtained.

The theoretical thickness of the calcium carbonate
layer is 20 nm.

The composite particle concentration of the
suspension is 5.2% by weight.

EXAMPLE 6

Preparation of composite particles.

The suspension obtained in Example 2 is dried using a Buchi atomizer. The temperature of entry is 207°C and that
5 at the exit 122°C.

A powder consisting of spherical composite particles made up of an organic polymer core covered with calcium carbonate is obtained.

EXAMPLE 7

10 Preparation of hollow particles according to the invention.

The powder obtained in Example 6 is calcined at 630°C, the rate of temperature rise being 3°C/min and the duration of the plateau at 630°C, 4 hours.

Hollow particles of calcium carbonate of diameter
15 smaller than 0.2 μm (by TEM) are thus obtained.



CLAIMS

1. Composite particles having mean diameter not exceeding 5 μm and comprising an organic polymer core at least partly covered with calcium carbonate.

5 2. Particles according to claim 1 wherein the calcium carbonate is in calcite form.

3. Particles according to claim 1 or 2 wherein the organic polymer is a styrene-butadiene copolymer containing carboxylate, sulphate or sulphonate functional groups or a
10 styrene-butadiene-acrylamide copolymer.

4. Particles according to claim 3 wherein the organic polymer has a carboxylate functional group content of from 1 to 50% by weight of ion-forming monomers present in the organic polymer and an amide functional group content
15 lower than 5% by weight of ion-forming monomers present in the organic polymer.

5. Particles according to any one of claims 1 to 4 wherein the glass transition temperature of the organic polymer is from -80°C to 200°C .

20 6. Hollow particles having a mean diameter not exceeding 5 μm and consisting of a calcium carbonate shell.

7. Particles according to any one of claims 1 to 6 wherein the thickness of the shell or of the layer of calcium carbonate does not exceed 200 nm.

25 8. Particles according to claim 7 wherein the thickness of the shell or of the layer of calcium carbonate is from 5 to 70 nm.

9. Particles according to any one of claims 1 to 8 which have a dispersion index not exceeding 0.50.

30 10. Particles according to claim 9 which have a dispersion index of less than 0.30.

11. Particles according to any one of claims 1 to 10 which have a mean diameter of from 0.1 to 0.3 μm .

12. Particles according to any one of claims 1
35 to 11 which have a specific surface of from 1 to 100 m^2/g .

13. A suspension of composite particles which comprises composite particles as defined in any one of claims 1 to 5 or 7 to 12.



14. A suspension of hollow particles which comprises hollow particles as defined in any one of claims 6 to 12.

15. A process for the preparation of a suspension
5 of composite particles as defined in claim 13 which comprises contacting a latex with calcium dihydroxide, and then adding carbon dioxide to the mixture to cause precipitation of the calcium carbonate on the latex particles.

16. A process according to claim 15 wherein a
10 stabilizer is added to the latex before it is placed in contact with the calcium dihydroxide.

17. A process according to claim 16 wherein 1 to 50g of stabilizer is added per kg of latex.

18. A process according to claim 17 wherein less
15 than 20g of stabilizer is added per kg of latex.

19. A process according to any one of claims 15 to 18 wherein an inhibitor of growth of calcium carbonate is introduced into the mixture of latex and calcium dihydroxide.

20. A process according to any one of claims 15
20 to 19 which is carried out at a temperature of from 20 to 40°C.

21. A process according to any one of claims 15 to 20 which further comprises an additional stage of maturing after the precipitation of calcium carbonate on the latex
25 particles.

22. A process for the preparation of composite particles as defined in any to one of claims 1 to 5 or 7 to 12 wherein a suspension obtained by a process as defined in any one of claims 15 to 21 is dried.

30 23. A process for the preparation of hollow particles as defined in any one of to claims 6 to 12 wherein composite particles as defined in any one of claims 1 to 5 or 7 to 12 or which have been obtained by a process as defined in claim 22 are calcined.

35 24. A process for the preparation of hollow particles as defined in any one of claims 6 to 12 wherein the composite particles as defined in any one of claims 1 to 5 or 7 to 12 or obtained by a process as defined in claim 22 are placed in a solvent for the organic polymer to



dissolve the organic polymer core, the mixture is centrifuged and the hollow particles obtained are dried.

25. Use of composite particles as defined in any one of claims 1 to 5 or 7 to 12 or of the particles obtained
5 by the process as defined in claim 22 as fillers or additives in plastics and in elastomers.

26. Use of hollow particles as defined in any one of claims 6 to 12 or of the particles obtained by the process as defined in claim 23 or 24 as fillers in elastomers.