

CORE/SHELL PARTICLES

The invention relates to granules or dispersions comprising core/shell particles, and to the core/shell particles and to processes for the preparation of the granules or dispersions or core/shell particles.

Patent Application WO 03/25035 discloses mouldings which essentially consist of core/shell particles whose shell forms a matrix and whose core is essentially solid and has an essentially monodisperse size distribution, where the shell is preferably strongly bonded to the core via an interlayer. The refractive indices of the core material and the shell material differ here, causing the said optical effect, preferably opalescence. In a preferred embodiment in accordance with WO 03/25035, the core of the core/shell particles consists of crosslinked polystyrene and the shell consists of a polyacrylate, preferably polyethyl acrylate, polybutyl acrylate, polymethyl methacrylate and/or a copolymer thereof.

According to Patent Application DE 10204338, contrast materials, such as pigments, may additionally be introduced into mouldings of such core/shell particles. The incorporated contrast materials effect an increase in brightness, contrast and depth of the observed colour effects in these mouldings.

There is nevertheless a demand for core/shell particles for photonic materials having optimised optical properties. In addition, the known core/shell particles are of only limited suitability for large-scale industrial processing by the usual methods in the polymer industry.

The object of the present invention was to provide core/shell particles which can be processed by large-scale industrial processing methods and/or have optimised optical properties.

The present invention therefore relates firstly to core/shell particles whose core is essentially solid and has an essentially monodisperse size distribution, where there is a difference between the refractive indices of the core material and the shell material, and the core consists of a material which is either not flowable or becomes flowable at a temperature above the melting point of the shell material, and the shell is bonded to the core via an inter-layer, characterised in that the shell consists of a copolymer which comprises at least one C₄-C₈-alkyl acrylate and at least one C₄-C₈-alkyl or -alkylaryl methacrylate as monomer units.

The present invention furthermore relates to granules comprising the core/shell particles according to the invention and optionally assistants and additives, and to dispersions comprising the core/shell particles according to the invention and at least one solvent or dispersion medium and optionally dispersion aids, and to corresponding preparation processes.

In a preferred variant of the invention, the shell of the core/shell particles comprises from 10 to 70% by weight, preferably from 25 to 60% by weight and particularly preferably from 35 to 55% by weight of C₄-C₈-alkyl acrylate, from 10 to 80% by weight, preferably from 25 to 70% by weight and particularly preferably from 35 to 60% by weight of C₄-C₈-alkyl or -alkylaryl methacrylate and from 0.5 to 40% by weight, preferably from 1 to 30% by weight and particularly preferably from 5 to 20% by weight of methyl methacrylate, in each case based on the weight ratio of the monomer units, as monomer units.

It is particularly preferred here for the at least one C₄-C₈-alkyl acrylate to be selected from the group consisting of n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, n-propyl acrylate, n-pentyl acrylate, n-hexyl acrylate, n-octyl acrylate, where the at least one C₄-C₈-alkyl acrylate is preferably n-butyl acrylate.

The at least one C₄-C₈-alkyl or -alkylaryl methacrylate is preferably selected from the group consisting of n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, n-propyl methacrylate, n-pentyl methacrylate, n-hexyl methacrylate, cyclohexyl methacrylate, n-octyl methacrylate, benzyl methacrylate, where the at least one C₄-C₈-alkyl acrylate is preferably n-butyl methacrylate.

In accordance with the invention, the shell is very particularly preferably formed from a random copolymer, which is preferably built up from n-butyl acrylate, n-butyl methacrylate and methyl methacrylate.

In particular, the core/shell particles according to the invention have the following advantages here:

- Dispersions of the core/shell particles according to the invention are shear-stable. The dispersions can be conveyed by pumping. No undesired coagulation takes place.
- The particles are approximately odour-neutral. Compared with core/shell particles having an ethyl acrylate-containing shell, which tend towards a pungent odour, the complex purification of the products from residual monomers is thus superfluous in the preparation. In practice, the removal of the ethyl acrylate residual monomers by post-initiation and polymerisation of the residual monomers results in a significant impairment of the processing properties of the ethyl acrylate-containing core/shell particles. This impairment can be avoided with the particles according to the invention.
- In addition, mouldings made from the particles according to the invention exhibit increased brightness of the colour effects.
- The mechanical load-bearing capacity of the mouldings which can be produced in accordance with the invention is improved compared with the prior art.

In a preferred embodiment of the invention, the interlayer is a layer of crosslinked or at least partially crosslinked polymers. The crosslinking of the interlayer here can take place via free radicals, for example induced by UV irradiation, or preferably via di- or oligofunctional monomers. Preferred interlayers in this embodiment comprise from 0.01 to 100% by weight, particularly preferably from 0.25 to 10% by weight, of di- or oligofunctional monomers. Preferred di- or oligofunctional monomers are, in particular, isoprene and allyl methacrylate (ALMA). Such an interlayer of crosslinked or at least partially crosslinked polymers preferably has a thickness in the range from 10 to 20 nm. If the interlayer comes out thicker, the refractive index of the layer is selected so that it corresponds either to the refractive index of the core or to the refractive index of the shell.

If copolymers which, as described above, contain a crosslinkable monomer are employed as interlayer, the person skilled in the art will have absolutely no problems in suitably selecting corresponding copolymerisable monomers. For example, corresponding copolymerisable monomers can be selected from a so-called Q-e-scheme (cf. textbooks on macromolecular chemistry). Thus, monomers such as methyl methacrylate and methyl acrylate can preferably be polymerised with ALMA.

In another, likewise preferred embodiment of the present invention, the shell polymers are grafted directly onto the core via a corresponding functionalisation of the core. The surface functionalisation of the core forms the interlayer according to the invention. The type of surface functionalisation here depends principally on the material of the core. Silicon dioxide surfaces, for example, can be suitably modified with silanes carrying correspondingly reactive end groups, such as epoxide functions or free double bonds. Other surface functionalisations, for example for metal oxides, may be titanates or organoaluminium compounds, each containing organic side chains with corresponding functions. In the case of polymeric cores, a styrene functionalised on the aromatic ring, such as bromostyrene, can, for

example, be employed for the surface modification. The grafting-on of the shell polymers can then be achieved via this functionalisation. In particular, the interlayer may also effect adhesion of the shell to the core via ionic interactions or complex bonds.

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The core of the core/shell particles consists of a material which is either not flowable or becomes flowable at a temperature above the melting point of the shell material. This can be achieved through the use of polymeric materials having a correspondingly high glass transition temperature (T_g), preferably crosslinked polymers, or through the use of inorganic core materials.

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In a preferred variant of the invention, the core consists of an inorganic material, preferably a metal or semimetal or a metal chalcogenide or metal pnictide. For the purposes of the present invention, the term chalcogenides is applied to compounds in which an element from group 16 of the Periodic Table is the electronegative bonding partner; the term pnictides is applied to those in which an element from group 15 of the Periodic Table is the electronegative bonding partner.

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Preferred cores consist of metal chalcogenides, preferably metal oxides, or metal pnictides, preferably nitrides or phosphides. For the purposes of these terms, the term metal is taken to mean all elements which can occur as electropositive partner compared with the counterions, such as the classical metals from the sub-groups, or the main-group metals from the first and second main groups, but equally well all elements from the third main group, as well as silicon, germanium, tin, lead, phosphorus, arsenic, antimony and bismuth. Preferred metal chalcogenides and metal pnictides include, in particular, silicon dioxide, aluminium oxide, gallium nitride, boron nitride, aluminium nitride, silicon nitride and phosphorus nitride.

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In a variant of the present invention, the starting material employed for the production of the core/shell particles according to the invention preferably comprises monodisperse cores of silicon dioxide, which can be obtained, for example, by the process described in US 4,911,903. The cores here are produced by hydrolytic polycondensation of tetraalkoxysilanes in an aqueous/ammoniacal medium, where firstly a sol of primary particles is produced, and the resultant SiO₂ particles are subsequently converted to the desired particle size by continuous, controlled, metered addition of tetraalkoxysilane. This process enables the production of monodisperse SiO₂ cores having mean particle diameters of between 0.05 and 10 µm with a standard deviation of 5%.

Preferred starting materials are furthermore SiO₂ cores which have been coated with (semi)metals or with metal oxides which are non-absorbent in the visible region, such as, for example, TiO₂, ZrO₂, ZnO₂, SnO₂ or Al₂O₃. The production of SiO₂ cores coated with metal oxides is described in greater detail in, for example, US 5,846,310, DE 198 42 134 and DE 199 29 109.

Another starting material which can be employed comprises monodisperse cores of non-absorbent metal oxides, such as TiO₂, ZrO₂, ZnO₂, SnO₂ or Al₂O₃, or metal-oxide mixtures. Their production is described, for example, in EP 0 644 914. Furthermore, the process described in EP 0 216 278 for the production of monodisperse SiO₂ cores can be applied readily and with the same result to other oxides. Tetraethoxysilane, tetrabutoxytitanium, tetrapropoxyzirconium or mixtures thereof are added in one portion with vigorous mixing to a mixture of alcohol, water and ammonia, whose temperature is set precisely to from 30 to 40°C by means of a thermostat, and the resultant mixture is stirred vigorously for a further 20 seconds, during which a suspension of monodisperse cores in the nanometre range forms. After a post-reaction time of from 1 to 2 hours, the cores are separated off in a conventional manner, for example by centrifugation, washed and dried.

Suitable starting materials for the production of the core/shell particles according to the invention are furthermore also monodisperse cores of polymers which contain included particles, for example metal oxides. Materials of this type are available, for example, from micro caps Entwicklungs- and Vertriebs GmbH in Rostock. Microencapsulations based on polyesters, polyamides and natural and modified carbohydrates are produced in accordance with customer-specific requirements.

It is furthermore possible to employ monodisperse cores of metal oxides which have been coated with organic materials, for example silanes. The monodisperse cores are dispersed in alcohols and modified with conventional organoalkoxysilanes. The silanisation of spherical oxide particles is also described in DE 43 16 814. The silanes preferably form the above-mentioned interlayer here.

For the intended use of the core/shell particles according to the invention for the production of mouldings, it is important that the shell material can be formed into a film, i.e. that it can be softened, viscoelastically plasticised or liquefied by simple measures to such an extent that the cores of the core/shell particles are at least able to form domains having a regular arrangement. The regularly arranged cores in the matrix formed by film formation of the shells of the core/shell particles form a diffraction grating, which causes interference phenomena and thus results in very interesting colour effects.

With regard to the possibility of varying the invention-relevant properties of the cores of the core/shell particles according to the invention as needed, however, it is often advantageous for the cores to comprise one or more polymers and/or copolymers (core polymers) or to consist of polymers of this type.

Therefore, in a variant of the invention, the cores particularly preferably consist of organic homo- or copolymers, which are preferably crosslinked.

5 The cores preferably comprise a single polymer or copolymer. It is particularly preferred in accordance with the invention for the core to consist of crosslinked polystyrene or a copolymer of methyl methacrylate and styrene.

10 With the use of polymer substances as core material, the person skilled in the art gains the freedom to determine their relevant properties, such as, for example, their composition, the particle size, the mechanical data, the refractive index, the glass transition temperature, the melting point and the core:shell weight ratio and thus also the applicational properties of the core/shell particles, which ultimately also affect the properties of the mouldings produced therefrom.

15 Polymers and/or copolymers which may be present in the core material or of which it consists are high-molecular-weight compounds which conform to the specification given above for the core material. Both polymers and copolymers of polymerisable unsaturated monomers and polycondensates
20 and copolycondensates of monomers containing at least two reactive groups, such as, for example, high-molecular-weight aliphatic, aliphatic/aromatic or fully aromatic polyesters, polyamides, polycarbonates, polyureas and polyurethanes, but also amino and phenolic resins, such as, for example, melamine-formaldehyde, urea-formaldehyde and phenol-formaldehyde condensates, are suitable.

25 For the preparation of epoxy resins, which are likewise suitable as core material, epoxide prepolymers, which are obtained, for example, by reaction of bisphenol A or other bisphenols, resorcinol, hydroquinone, hexane-
30 diol or other aromatic or aliphatic diols or polyols, or phenol-formaldehyde condensates, or mixtures thereof with one another, with epichlorohydrin or

other di- or polyepoxides, are usually mixed with further condensation-capable compounds directly or in solution and allowed to cure.

5 In a preferred variant of the invention, the polymers of the core material are advantageously crosslinked (co)polymers, since these usually only exhibit their glass transition at high temperatures. These crosslinked polymers may either already have been crosslinked during the polymerisation or polycondensation or copolymerisation or copolycondensation or may have been post-crosslinked in a separate process step after the actual
10 (co)polymerisation or (co)polycondensation.

With regard to the ability of the core/shell particles to be converted into mouldings, it is advantageous for the core:shell weight ratio to be in the range from 2:1 to 1:5, preferably in the range from 3:2 to 1:3 and particularly preferably in the range less than 1.2:1. In specific embodiments of the
15 present invention, it is even preferred for the core:shell weight ratio to be less than 1:1, with a typical upper limit of the shell proportion being at a core:shell weight ratio of 2:3.

20 The core/shell particles according to the invention can be produced by various processes. The present invention furthermore relates to a preferred way of obtaining the particles. This is a process for the preparation of dispersions of core/shell particles by a) surface treatment of monodisperse cores, and b) application of the shell comprising organic polymers to the
25 treated cores.

In a process variant, the monodisperse cores are obtained by emulsion polymerisation in a step a).

30 In a preferred variant of the invention, a crosslinked polymeric interlayer, which preferably has reactive centres to which the shell can be covalently

bonded, is applied to the cores, preferably by emulsion polymerisation or by ATR polymerisation, in step b). ATR polymerisation here stands for atom transfer radical polymerisation, as described, for example, in K. Matyjaszewski, Practical Atom Transfer Radical Polymerization, Polym. Mater. Sci. Eng. 2001, 84. The encapsulation of inorganic materials by means of ATRP is described, for example, in T. Werne, T. E. Patten, Atom Transfer Radical Polymerization from Nanoparticles: A Tool for the Preparation of Well-Defined Hybrid Nanostructures and for Understanding the Chemistry of Controlled/"Living" Radical Polymerization from Surfaces, J. Am. Chem. Soc. 2001, 123, 7497-7505 and WO 00/11043. The performance both of this method and of emulsion polymerisations is familiar to the person skilled in the art of polymer preparation and is described, for example, in the above-mentioned literature references.

Accordingly, a process for the preparation of dispersions in which the monodisperse cores are obtained by emulsion polymerisation in a step a1), and a crosslinked polymeric interlayer, which preferably has reactive centres to which the shell can be covalently bonded, is applied to the cores, preferably by emulsion polymerisation or by ATR polymerisation, in a step a2), is a preferred variant of the process according to the invention.

The liquid reaction medium in which the polymerisations or copolymerisations can be carried out consists of the solvents, dispersion media or diluents usually employed in polymerisations, in particular in emulsion polymerisation processes. The choice here is made in such a way that the emulsifiers employed for homogenisation of the core particles and shell precursors are able to develop adequate efficacy. Suitable liquid reaction media for carrying out the process according to the invention are aqueous media, in particular water.

Suitable for initiation of the polymerisation are, for example, polymerisation initiators which decompose either thermally or photochemically, form free

radicals and thus initiate the polymerisation. Preferred thermally activatable polymerisation initiators here are those which decompose at between 20 and 180°C, in particular between 20 and 80°C. Particularly preferred polymerisation initiators are peroxides, such as dibenzoyl peroxide, di-tert-butyl peroxide, peresters, percarbonates, perketals, hydroperoxides, but also inorganic peroxides, such as H_2O_2 , salts of peroxosulfuric acid and peroxodisulfuric acid, azo compounds, alkylboron compounds, and hydrocarbons which decompose homolytically. The initiators and/or photoinitiators, which, depending on the requirements of the polymerised material, are employed in amounts of between 0.01 and 15% by weight, based on the polymerisable components, can be used individually or, in order to utilise advantageous synergistic effects, in combination with one another. In addition, use is made of redox systems, such as, for example, salts of peroxodisulfuric acid and peroxosulfuric acid in combination with low-valency sulfur compounds, particularly ammonium peroxodisulfate in combination with sodium dithionite.

Corresponding processes have also been described for the preparation of polycondensation products. Thus, it is possible for the starting materials for the preparation of polycondensation products to be dispersed in inert liquids and condensed, preferably with removal of low-molecular-weight reaction products, such as water or – for example on use of di(lower alkyl) dicarboxylates for the preparation of polyesters or polyamides – lower alkanols.

Polyaddition products are obtained analogously by reaction of compounds which contain at least two, preferably three, reactive groups, such as, for example, epoxide, cyanate, isocyanate or isothiocyanate groups, with compounds carrying complementary reactive groups. Thus, isocyanates react, for example, with alcohols to give urethanes, with amines to give urea derivatives, while epoxides react with these complementary groups to give hydroxyethers and hydroxylamines respectively. Like the polycondensa-

tions, polyaddition reactions can also advantageously be carried out in an inert solvent or dispersion medium.

It is also possible for aromatic, aliphatic or mixed aromatic/aliphatic polymers, for example polyesters, polyurethanes, polyamides, polyureas, polyepoxides or also solution polymers, to be dispersed or emulsified (secondary dispersion) in a dispersion medium, such as, for example, in water, alcohols, tetrahydrofuran or hydrocarbons, and to be post-condensed, crosslinked and cured in this fine distribution.

The stable dispersions required for these polymerisation, polycondensation or polyaddition processes are generally prepared using dispersion aids besides the solvents or dispersion media.

The dispersion aids used are preferably water-soluble, high-molecular-weight organic compounds containing polar groups, such as polyvinylpyrrolidone, copolymers of vinyl propionate or acetate and vinylpyrrolidone, partially saponified copolymers of an acrylate and acrylonitrile, polyvinyl alcohols having different residual acetate contents, cellulose ethers, gelatine, block copolymers, modified starch, low-molecular-weight polymers containing carboxyl and/or sulfonyl groups, or mixtures of these substances, where the proportion of dispersion aid in the dispersion is preferably in the range from 0.01 to 10% by weight, particularly preferably in the range from 0.5 to 5% by weight.

Particularly preferred protective colloids are polyvinyl alcohols having a residual acetate content of less than 35 mol%, in particular from 5 to 39 mol%, and/or vinylpyrrolidone-vinyl propionate copolymers having a vinyl ester content of less than 35% by weight, in particular from 5 to 30% by weight.

It is possible to use nonionic or ionic emulsifiers, if desired also as a mixture. Preferred emulsifiers are ethoxylated or propoxylated, relatively long-chain alkanols or alkylphenols having different degrees of ethoxylation or propoxylation (for example adducts with from 0 to 50 mol of alkylene oxide) or neutralised, sulfated, sulfonated or phosphated derivatives thereof. Also particularly suitable are neutralised dialkylsulfosuccinic acid esters or alkyl-diphenyl oxide disulfonates, where the use of nonionic emulsifiers and in particular the use of ethoxylated alkylphenols is preferred. As an example thereof, mention may be made of the octylphenol ethoxylates available under the trade name Triton™ (Dow Chemicals).

Particularly advantageous are combinations of these emulsifiers with the above-mentioned protective colloids, since particularly finely divided dispersions are obtained therewith. Dispersions comprising at least one non-ionic or ionic emulsifier and at least one protective colloid are therefore particularly preferred in accordance with the invention.

Special processes for the production of monodisperse polymer particles have also already been described in the literature (for example R.C. Backus, R.C. Williams, J. Appl. Physics 19, p. 1186 (1948)) and can advantageously be employed, in particular, for the production of the cores. It need merely be ensured here that the above-mentioned particle sizes are observed. A further aim is the greatest possible uniformity of the polymers. The particle size in particular can be set via the choice of suitable emulsifiers and/or protective colloids or corresponding amounts of these compounds.

Through the setting of the reaction conditions, such as temperature, pressure, reaction duration and use of suitable catalyst systems, which influence the degree of polymerisation in a known manner, and the choice of the monomers employed for their preparation – in terms of type and pro-

portion – the desired property combinations of the requisite polymers can be set specifically. The particle size can be set, for example, via the choice and amount of the initiators and other parameters, such as the reaction temperature. The corresponding setting of these parameters presents the person skilled in the art in the area of polymerisation with no difficulties at all.

In particular on use of inorganic cores, it may also be preferred for the core to be subjected to pre-treatment which enables bonding of the shell before the shell is polymerised on. This can usually consist in chemical functionalisation of the particle surface, as is known from the literature for a very wide variety of inorganic materials. It may particularly preferably involve application to the surface of chemical functions which, as reactive chain end, enable grafting-on of the shell polymers. Examples which may be mentioned in particular here are terminal double bonds, epoxy functions and polycondensable groups. The functionalisation of hydroxyl-carrying surfaces with polymers is disclosed, for example, in EP-A-337 144. Further methods for the modification of particle surfaces are well known to the person skilled in the art and are described, for example, in various textbooks, such as Unger, K.K., Porous Silica, Elsevier Scientific Publishing Company (1979).

The present invention furthermore relates to a process for the preparation of granules comprising core/shell particles in which a dispersion is dried and compounded.

The drying here can be carried out by means of conventional methods, such as, for example, spray drying, fluidised-bed drying or freeze drying.

The granules according to the invention may, if it is technically advantageous, comprise assistants and additives here. They can serve for opti-

5 mum setting of the applicational data or properties desired or necessary for application and processing. Examples of assistants and/or additives of this type are antioxidants, UV stabilisers, biocides, plasticisers, film-formation assistants, flow-control agents, fillers, melting assistants, adhesives, release agents, application assistants, demoulding assistants and viscosity modifiers, for example thickeners.

10 Particularly recommended are additions of film-formation assistants and film modifiers based on compounds of the general formula $\text{HO-C}_n\text{H}_{2n}\text{-O-(C}_n\text{H}_{2n}\text{-O)}_m\text{H}$, in which n is a number from 2 to 4, preferably 2 or 3, and m is a number from 0 to 500. The number n can vary within the chain, and the various chain members can be incorporated in a random or blockwise distribution. Examples of assistants of this type are ethylene glycol, propylene glycol, di-, tri- and tetraethylene glycol, di-, tri- and tetrapropylene glycol, 15 polyethylene oxides, polypropylene oxide and ethylene oxide-propylene oxide copolymers having molecular weights up to about 15,000 and a random or block-like distribution of the ethylene oxide and propylene oxide groups.

20 If desired, organic or inorganic solvents, dispersion media or diluents, which, for example, extend the open time of the formulation, i.e. the time available for its application to substrates, waxes or hot-melt adhesives are also possible as additives.

25 If desired, stabilisers against UV radiation and weathering influences can also be added to the granules. Suitable for this purpose are, for example, derivatives of 2,4-dihydroxybenzophenone, derivatives of 2-cyano-3,3'-diphenyl acrylate, derivatives of 2,2',4,4'-tetrahydroxybenzophenone, derivatives of o-hydroxyphenylbenzotriazole, salicylic acid esters, o-hydroxyphenyl-s-triazines or sterically hindered amines. These substances may 30 likewise be employed individually or in the form of a mixture.

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The total amount of assistants and/or additives is up to 40% by weight, preferably up to 20% by weight, particularly preferably up to 5% by weight, of the weight of the granules. Accordingly, the granules consist of at least 60% by weight, preferably at least 80% by weight and particularly preferably at least 95% by weight, of core/shell particles.

The present invention furthermore relates to mouldings having an optical effect obtainable from the core/shell particles or granules described above, and to the use of core/shell particles or granules of this type for the production of mouldings.

For the purposes of the invention, the term optical effect is taken to mean both effects in the visible wavelength region of light and, for example, also effects in the UV or infrared region. It has recently become customary to refer to effects of this type in general as photonic effects. All these effects are optical effects for the purposes of the present invention, where, in a preferred embodiment, the effect is opalescence in the visible region. In the sense of a conventional definition of the term, the mouldings obtainable from the core/shell particles according to the invention are photonic crystals (cf. Nachrichten aus der Chemie; 49(9) September 2001; pp. 1018 - 1025).

In a preferred variant of the production of mouldings according to the invention, the temperature in step a) is at least 40°C, preferably at least 60°C, above the glass transition temperature of the shell of the core/shell particles. It has been found empirically that the flowability of the shell in this temperature range meets the requirements for economical production of the mouldings to a particular extent.

In a likewise preferred process variant which results in the mouldings according to the invention, the flowable core/shell particles are cooled

under the action of the mechanical force from b) to a temperature at which the shell is no longer flowable.

For the purposes of the present invention, the action of mechanical force can be the action of a force which occurs in the conventional processing steps of polymers. In preferred variants of the present invention, the action of mechanical force takes place either:

- by uniaxial pressing or
- the action of force during an injection-moulding operation or
- during a transfer moulding operation,
- during (co)extrusion or
- during a calendering operation or
- during a blowing operation.

If the action of force takes place by uniaxial pressing, the mouldings according to the invention are preferably films. Films according to the invention can preferably also be produced by calendering, film blowing or flat-film extrusion. The various ways of processing polymers under the action of mechanical forces are well known to the person skilled in the art and are revealed, for example, by the standard textbook Adolf Franck, "Kunststoff-Kompendium" [Plastics Compendium]; Vogel-Verlag; 1996.

If mouldings are produced by injection moulding, it is particularly preferred for the demoulding not to be carried out until the mould has cooled with the moulding present therein. When implemented industrially, it is advantageous here to employ moulds having a large cooling channel cross section, since the cooling can then take place in a shorter time. It has been found that cooling in the mould makes the colour effects according to the invention significantly more intense. It is assumed that better arrangement of the core/shell particles to form a lattice occurs during this uniform cooling

process. It is particularly advantageous here for the mould to be heated before the injection operation.

5 In order to achieve the optical or photonic effect according to the invention, it is desirable for the core/shell particles to have a mean particle diameter in the range from about 5 nm to about 2000 nm. It may be particularly preferred here for the core/shell particles to have a mean particle diameter in the range from about 5 to 20 nm, preferably from 5 to 10 nm. In this case, the cores may be known as "quantum dots"; they exhibit the corresponding
10 effects known from the literature. In order to achieve colour effects in the region of visible light, it is particularly advantageous for the core/shell particles to have a mean particle diameter in the range about 50 – 500 nm. Particular preference is given to the use of particles in the range 100 – 500 nm since, in particles in this size range (depending on the refractive
15 index contrast which can be achieved in the photonic structure), the reflections of various wavelengths of visible light differ significantly from one another, and thus the opalescence which is particularly important for optical effects in the visible region occurs to a particularly pronounced extent in a very wide variety of colours. However, it is also preferred in a variant of the
20 present invention to employ multiples of this preferred particle size, which then result in reflections corresponding to the higher orders and thus in a broad colour play.

25 A further crucial factor for the intensity of the observed effects is the difference between the refractive indices of core and shell. Mouldings according to the invention preferably have a difference between the refractive indices of the core material and the shell material of at least 0.001, preferably at least 0.01 and particularly preferably at least 0.1.

30 In a particular embodiment of the invention, further nanoparticles are incorporated into the matrix phase of the mouldings in addition to the cores of the core/shell particles. These particles are selected with respect to their

particle size in such a way that they fit into the cavities of the sphere packing of the cores and thus cause only little change in the arrangement of the cores. Through specific selection of corresponding materials and/or the particle size, it is firstly possible to modify the optical effects of the mouldings, for example to increase their intensity. Secondly, it is possible through incorporation of suitable "quantum dots" to functionalise the matrix correspondingly. Preferred materials are inorganic nanoparticles, in particular nanoparticles of metals or of II-VI or III-V semiconductors or of materials which influence the magnetic/electrical (electronic) properties of the materials. Examples of preferred nanoparticles are noble metals, such as silver, gold and platinum, semiconductors or insulators, such as zinc chalcogenides and cadmium chalcogenides, oxides, such as haematite, magnetite or perovskite, or metal pnictides, for example gallium nitride, or mixed phases of these materials.

The precise mechanism which results in the uniform orientation of the core/shell particles in the mouldings according to the invention was hitherto unknown. However, it has been found that the action of a force is essential for the formation of the far-reaching order. It is assumed that the elasticity of the shell material under the processing conditions is crucial for the ordering process. The chain ends of the shell polymers generally attempt to adopt a coiled shape. If two particles come too close, the coils are compressed in accordance with the model concept, and repellent forces arise. Since the shell-polymer chains of different particles also interact with one another, the polymer chains are stretched in accordance with the model if two particles move away from one another. Due to the attempts by the shell-polymer chains to re-adopt a coiled shape, a force arises which pulls the particles closer together again. In accordance with the model concept, the far-reaching order of the particles in the moulding is caused by the interplay of these forces.

The invention furthermore relates to the use of mouldings according to the invention or of core/shell particles according to the invention for the preparation of pigments. The pigments obtainable in this way are particularly suitable for use in paints, coatings, printing inks, plastics, ceramics, glasses and cosmetic formulations. For this purpose, they can also be employed mixed with commercially available pigments, for example inorganic and organic absorption pigments, metal-effect pigments and LC pigments. The particles according to the invention are furthermore also suitable for the preparation of pigment compositions and for the preparation of dry preparations, such as, for example, granules. Pigment particles of this type preferably have a flake-form structure with an average particle size of 5 μm – 5 mm.

The pigments can be prepared, for example, by firstly producing a film from the core/shell particles, which may optionally be cured. The film can subsequently be comminuted in a suitable manner by cutting or crushing and, if desired, subsequent grinding to give pigments of suitable size. This operation can be carried out, for example, in a continuous belt process.

The pigment according to the invention can then be used for pigmenting surface coatings, powder coatings, paints, printing inks, plastics and cosmetic formulations, such as, for example, lipsticks, nail varnishes, cosmetic sticks, compact powders, make-up, shampoos and loose powders and gels.

The concentration of the pigment in the application system to be pigmented is generally between 0.1 and 70% by weight, preferably between 0.1 and 50% by weight and in particular between 1.0 and 20% by weight, based on the total solids content of the system. It is generally dependent on the specific application. Plastics usually comprise the pigment according to the invention in amounts of from 0.01 to 50% by weight, preferably from 0.01 to 25% by weight, in particular from 0.1 to 7% by weight, based on the plastic

composition. In the coatings area, the pigment mixture is employed in amounts of from 0.1 to 30% by weight, preferably from 1 to 10% by weight, based on the coating dispersion. In the pigmentation of binder systems, for example for paints and printing inks for gravure printing, offset printing or screen printing, or as precursor for printing inks, for example in the form of highly pigmented pastes, granules, pellets, etc., pigment mixtures with spherical colorants, such as, for example, TiO_2 , carbon black, chromium oxide, iron oxide, and organic "coloured pigments", have proven particularly suitable. The pigment is generally incorporated into the printing ink in amounts of 2-35% by weight, preferably 5-25% by weight and in particular 8-20% by weight. Offset printing inks can comprise the pigment in amounts of up to 40% by weight or more. The precursors for printing inks, for example in the form of granules, as pellets, briquettes, etc., comprise up to 95% by weight of the pigment according to the invention in addition to the binder and additives. The invention thus also relates to formulations which comprise the pigment according to the invention.

The following examples are intended to explain the invention in greater detail without limiting it.

Examples

Example 1: Preparation of dispersions of core/shell particles

Weight [g]		Notes
	Starting mixture	
11.1	1,4-butanediol diacrylate (BDDA)	
99.4	styrene	
1.38	sodium disulfite	in 40 ml of demineralised H ₂ O
4.2	dodecyl sulfate sodium salt (NaDS)	Texapon™ K12, addition as 15% solution/27.95 g
6060	demineralised water	
	Initiator 1	
10.36	sodium peroxodisulfate 100%	as 20.8% soln./49.8 ml
1.41	sodium disulfite 100%	as 3.4% soln./41.5 ml
		stir for 15 min
	Solution 1	
221.7	1,4-butanediol diacrylate (BDDA)	addition of solution 1 in 95 min
2011.3	styrene	
4.25	potassium hydroxide	
10.3	dodecyl sulfate sodium salt (NaDS)	Texapon™ K12, addition as 15% solution/68.75 g
2945	demineralised water	post-stirring time 10 min
	Initiator 2	
2.66	sodium peroxodisulfate	as 6.3% soln./42.2 ml
		post-stirring time 10 min

	Solution 2	
41.4	allyl methacrylate (AMA)	addition of solution 2 in 20 min
372.8	methyl methacrylate (MMA)	
2.1	dodecyl sulfate sodium salt (NaDS)	Texapon™ K12, addition as 15% solution/13.78 g
538	demineralised water	post-stirring time 20 min
	Solution 3	
374.8	methyl methacrylate (MMA)	addition of solution 3 over the course of 133 min
1761.79	butyl acrylate (n-BA)	
1611.8	butyl methacrylate (n-BMA)	
10.3	dodecyl sulfate sodium salt (NaDS)	Texapon™ K12, addition as 15% solution/68.4 g
9.3	Triton™ X405 (70%)	addition as 15% solution/ 43.4 g
3633	demineralised water	post-stirring time 30 min
	Post-stabilisation	
279 g	Triton™ X405 (70%)	corr. to 195 g of pure Triton™ X405

Triton™ X405 is an octylphenol ethoxylate having an average number of 35 ethylene oxide recurring units (commercial product from The Dow Chemical Company).

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Description of the procedure:

A water bath connected to a jacketed reactor is heated to 75°C.

6060 g of demineralised water and 27.95 g of Texapon™ K12 (15%) are introduced into a 20 l jacketed reactor fitted with impeller stirrer, and the reactor is flushed with nitrogen. 11.1 g of BDDA and 99.4 g of styrene are additionally added to the starting mixture.

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The reactor is then heated with stirring. 1.38 g of NaHS are dissolved in 40 ml of demineralised water at about 32°C and added to the starting mixture. During this operation, the reactor is again flushed with nitrogen.

At 55°C – 58°C, 49.8 ml of NaPS (20.8%) and 41.5 ml of NaHS (3.4%) are injected into the reactor, and the reaction is initiated.

After 15 minutes, a monomer emulsion consisting of 221.7 g of BDDA, 2011.3 g of styrene, 68.75 g of Texapon™ K12 (15%), 4.25 g of potassium hydroxide and 2945 ml of demineralised water (flushed with N₂) is metered in continuously over the course of 95 minutes via a membrane pump.

When the metered addition is complete, the mixture is stirred for a further 10 minutes.

42.2 ml of NaPS (6.3%) are then added. After 10 minutes, the second monomer mixture, consisting of 372.8 g of MMA, 41.4 g of AMA, 13.78 g of Texapon™ K12 (15%) and 538 g of demineralised water, is metered in continuously over the course of 20 minutes via a membrane pump.

After the metered addition, the mixture is stirred here for a further 20 minutes.

After completion of the post-stirring time, the third monomer mixture is metered in continuously over the course of 135 minutes via a membrane pump. The third monomer mixture consists of 1761.79 g of n-BA, 374.8 g of MMA, 1611.8 g of n-BMA, 68.4 g of Texapon™ K12 (15%), 43.4 g of Triton™ X405 (15%) and 3633 g of demineralised water.

The process temperature during the addition of all three monomer mixtures is 75°C.

After completion of the metered addition, the mixture is stirred for a further 30 minutes and slowly cooled to RT. During the cooling, the dispersion is

slowly re-stabilised with 5% of Triton™ X405 (based on the solids content, i.e. 195 g of Triton™ X405, i.e. 279 g of 70% Triton™ X405 solution).

The dispersion is filtered through a nylon gauze at < 40°C.

5 The resultant particles have a shell polymer composition of 10% by weight of MMA, 47% by weight of n-BA and 43% by weight of n-BMA. Core/shell particles having varied weight ratios of the shell polymer constituents to one another can be obtained analogously by variation of the monomer proportions.

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Example 2: Preparation of granules of the core/shell particles

15 3 kg of the core/shell particles from Example 1 are comminuted in a cutting mill (Rapid, model: 1528) with ice-cooling and subsequently compounded in a single-screw extruder (Plasti-Corder; Brabender; screw diameter 19 mm with 1-hole die (3 mm)). After a cooling zone, the compound is granulated in an A 90-5 granulator (Automatik).

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Example 3a: Production of a film from core/shell particles

25 2 g of the granules from Example 2 are heated to a temperature of 120°C without pressure in a Collin 300P press and pressed at a pressure of 30 bar to give a film. After cooling to room temperature, the pressure is reduced again.

Example 3b: Production of a film from core/shell particles

25 g of the granules from Example 2 are heated to a temperature of 150°C without pressure in a press with cassette cooling system (Dr. Collin GmbH; model: 300E) and pressed at a pressure of 250 bar to give a film. After cooling to room temperature, the pressure is reduced again after 8 minutes.

Example 4: Production of mouldings by injection moulding

0.2% by weight of release agent (Ceridust® 3615; Clariant) is admixed with the granules from Example 2. The mixture is processed further using a Klöckner Ferromatik 75 FX 75-2F injection-moulding machine, with the granules being injected into the mould, held at 80°C, at 900 bar and at a barrel temperature of 190°C, subsequently cooled in the mould and demoulded at a mould temperature of 30°C, giving mouldings having an optical effect which is dependent on the viewing angle.

Example 5: Production of a flat film (tape)

Granules from Example 2 are processed in a flat-film machine consisting of a single-screw extruder (Göttfert; model: Extrusimeter; screw diameter 20 mm; L/D 25), a thickness-adjustable film mould (width 135 mm) and a heatable smoothing stack (Leistritz; roll diameter 15 mm; roll width 350 mm). A film tape having a width of 125 mm and a thickness of 1 mm is obtained.

Comparative Example A: Production of core/shell particles having a butyl acrylate shell

A starting mixture, held at 4°C, consisting of 217 g of water, 0.4 g of butanediol diacrylate (Merck, destabilised), 3.6 g of styrene (BASF, destabilised) and 80 mg of sodium dodecylsulfate (SDS; Merck) is introduced into a stirred-tank reactor, pre-heated to 75°C, fitted with propeller stirrer, argon protective-gas inlet and reflux condenser, and dispersed with vigorous stirring. Immediately after the introduction, the reaction is initiated by directly successive addition of 50 mg of sodium dithionite (Merck), 250 mg of ammonium peroxodisulfate (Merck) and a further 50 mg of sodium dithionite (Merck), each dissolved in 5 g of water. After 10 min, a monomer emulsion comprising 6.6 g of butanediol diacrylate (Merck, destabilised), 59.4 g of styrene (BASF, destabilised), 0.3 g of SDS, 0.1 g of KOH and 90 g of water is metered in continuously over a period of 210 min. The reactor contents are stirred without further addition for 30 min. A second monomer emulsion comprising 3 g of allyl methacrylate (Merck, destabilised), 27 g of methyl methacrylate (BASF, destabilised), 0.15 g of SDS (Merck) and 40 g of water is subsequently metered in continuously over a period of 90 min. The reactor contents are subsequently stirred without further addition for 30 min. A monomer emulsion comprising 130 g of butyl acrylate (Merck, destabilised), 139 g of water and 0.33 g of SDS (Merck) is subsequently metered in continuously over a period of 180 min. For virtually complete reaction of the monomers, the mixture is subsequently stirred for a further 60 min. The core/shell particles are subsequently precipitated in 1 l of methanol, 1 l of dist. water is added, and the particles are filtered off with suction, dried and processed further as described in Examples 2 to 5.

Comparative Example B: Production of core/shell particles having a ethyl acrylate-butyl acrylate shell

A starting mixture, held at 4°C, consisting of 217 g of water, 0.4 g of butanediol diacrylate (Merck, destabilised), 3.6 g of styrene (BASF, destabilised) and 60 mg of sodium dodecylsulfate (SDS; Merck) is introduced into a stirred-tank reactor, pre-heated to 75°C, fitted with propeller stirrer, argon protective-gas inlet and reflux condenser, and dispersed with vigorous stirring. Immediately after the introduction, the reaction is initiated by directly successive addition of 50 mg of sodium dithionite (Merck), 300 mg of ammonium peroxodisulfate (Merck) and a further 50 mg of sodium dithionite (Merck), each dissolved in 5 g of water. After 10 min, a monomer emulsion comprising 8.1 g of butanediol diacrylate (Merck, destabilised), 72.9 g of styrene (BASF, destabilised), 0.375 g of SDS, 0.1 g of KOH and 110 g of water is metered in continuously over a period of 150 min. The reactor contents are stirred without further addition for 30 min. A second monomer emulsion comprising 1.5 g of allyl methacrylate (Merck, destabilised), 13.5 g of methyl methacrylate (BASF, destabilised), 0.075 g of SDS (Merck) and 20 g of water is subsequently metered in continuously over a period of 45 min. The reactor contents are subsequently stirred without further addition for 30 min. 50 mg of APS dissolved in 5 g of water are subsequently added. A monomer emulsion comprising 59.4 g of ethyl acrylate (MERCK, destabilised), 59.4 g of butyl acrylate, 1.2 g of acrylic acid, 120 g of water and 0.33 g of SDS (Merck) is subsequently metered in continuously over a period of 240 min. For virtually complete reaction of the monomers, the mixture is subsequently stirred for a further 60 min. The core/shell particles are subsequently precipitated in 1 l of methanol, 1 l of dist. water is added, and the particles are filtered off with suction and dried and processed further as described in Examples 2 to 5.

Example 6: Tensile and elongation experiments

In a tensile experiment, standardised test specimens are clamped between two clamp jaws and stretched: length of the parallel section of the test specimens about 20 mm; length of the measurement section: 25 mm; elongation measurement means: traverse with clamped length 30 mm; test speed: 20 mm/min; force measurement head: 1000 N; the preliminary force was 0.05 MPa. The force acting is based on the smallest cross sectional area of the test specimen and quoted as tensile stress.

Shell structure	Tensile strength/MPa	Modulus of elasticity/MPa	Elongation/%	Yield stress/MPa	Elongation at break/%
53.5% n-BMA, 36.5% n-BA, 10% MMA	4.00	24	57.6	3.77	174
43% n-BMA, 47% n-BA, 10% MMA	2.00	12	38.0	2.00	449
Comparative example 90% EA 10% MMA	0.70	~ 2	50.6	0.68	648

It can be seen that the particles according to the invention have a greater modulus of elasticity and only deform at a higher yield stress.

Patent Claims

- 1) Core/shell particles whose core is essentially solid and has an essentially monodisperse size distribution, where there is a difference between the refractive indices of the core material and the shell material, and the core consists of a material which is either not flowable or becomes flowable at a temperature above the melting point of the shell material, and the shell is bonded to the core via an interlayer, characterised in that the shell consists of a copolymer which comprises at least one C₄-C₈-alkyl acrylate and at least one C₄-C₈-alkyl or -alkylaryl methacrylate as monomer units.
- 2) Core/shell particles according to Claim 1, characterised in that the shell comprises
- (a) from 10 to 70% by weight, preferably from 25 to 60% by weight and particularly preferably from 35 to 55% by weight of C₄-C₈-alkyl acrylate,
- (b) from 10 to 80% by weight, preferably from 25 to 70% by weight and particularly preferably from 35 to 60% by weight of C₄-C₈-alkyl or -alkylaryl methacrylate,
- (c) from 0.5 to 40% by weight, preferably from 1 to 30% by weight and particularly preferably from 5 to 20% by weight of methyl methacrylate,
- in each case based on the weight ratio of the monomer units, as monomer units.
- 3) Core/shell particles according to at least one of Claims 1 or 2, characterised in that the at least one C₄-C₈-alkyl acrylate is selected from the group consisting of n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, n-propyl acrylate, n-pentyl acrylate, n-hexyl acrylate, n-octyl

acrylate, where the at least one C₄-C₈-alkyl acrylate is preferably n-butyl acrylate.

- 5 4) Core/shell particles according to at least one of the preceding claims, characterised in that the at least one C₄-C₈-alkyl or -alkylaryl methacrylate is selected from the group consisting of n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, n-propyl methacrylate, n-pentyl methacrylate, n-hexyl methacrylate, cyclohexyl methacrylate, n-octyl methacrylate, benzyl methacrylate, where the at least one
- 10 C₄-C₈-alkyl acrylate is preferably n-butyl methacrylate.
- 15 5) Core/shell particles according to at least one of the preceding claims, characterised in that the shell is formed by a random copolymer, which is preferably built up from n-butyl acrylate, n-butyl methacrylate and methyl methacrylate.
- 20 6) Core/shell particles according to at least one of the preceding claims, characterised in that the shell is grafted onto the core via an at least partially crosslinked interlayer.
- 25 7) Core/shell particles according to at least one of the preceding claims, characterised in that the core consists of an organic polymer, which is preferably crosslinked, where the core particularly preferably consists of crosslinked polystyrene or a copolymer of methyl methacrylate and styrene.
- 30 8) Core/shell particles according to at least one of Claims 1 to 6, characterised in that the core consists of an inorganic material, preferably a metal or semimetal or a metal chalcogenide or metal pnictide, particularly preferably silicon dioxide.

- 5
- 9) Core/shell particles according to at least one of the preceding claims, characterised in that the core/shell particles have a mean particle diameter in the range from about 5 nm to about 2000 nm, preferably in the range from about 5 to 20 nm or in the range 100 – 500 nm.
- 10
- 10) Core/shell particles according to at least one of the preceding claims, characterised in that the core:shell weight ratio is in the range from 2:1 to 1:5, preferably in the range from 3:2 to 1:3 and particularly preferably in the range less than 1.2:1.
- 15
- 11) Core/shell particles according to at least one of the preceding claims, characterised in that the difference between the refractive indices of the core material and the shell material is at least 0.001, preferably at least 0.01 and particularly preferably at least 0.1.
- 20
- 12) Granules comprising core/shell particles according to at least one of Claims 1 to 11 and optionally assistants and additives.
- 25
- 13) Granules according to Claim 12, characterised in that present as assistant and additive is at least one compound selected from the groups consisting of antioxidants, UV stabilisers, biocides, plasticisers, film-formation assistants, flow-control agents, fillers, melting assistants, adhesives, release agents, application assistants, demoulding assistants, viscosity modifiers, such as, for example, thickeners.
- 30
- 14) Granules according to at least one of the preceding claims, characterised in that assistants and additives are present in amounts of up to 40% by weight, preferably up to 20% by weight, particularly preferably up to 5% by weight, based on the weight of the granules.

- 15) Granules according to at least one of the preceding claims, characterised in that present as assistant and additive is least one compound selected from the film-formation assistants and film modifiers, preferably based on compounds of the general formula $\text{HO-C}_n\text{H}_{2n}\text{-O-(C}_n\text{H}_{2n}\text{-O)}_m\text{H}$, in which n is a number from 2 to 4, preferably 2 or 3, and m is a number from 0 to 500, where ethylene glycol, propylene glycol, di-, tri- and tetraethylene glycol, di-, tri- and tetrapropylene glycol, polyethylene oxides, polypropylene oxide and ethylene oxide-propylene oxide copolymers having molecular weights up to about 15,000 and a random or block-like distribution of the ethylene oxide and propylene oxide groups are particularly preferred.
- 16) Granules according to at least one of the preceding claims, characterised in that present as assistant and additive is at least one compound selected from the stabilisers against UV radiation and weathering influences, preferably selected from the group consisting of the derivatives of 2,4-dihydroxybenzophenone, derivatives of 2-cyano-3,3'-diphenyl acrylate, derivatives of 2,2',4,4'-tetrahydroxybenzophenone, derivatives of o-hydroxyphenylbenzotriazole, salicylates, o-hydroxyphenyl-s-triazines and sterically hindered amines, and mixtures of these compounds.
- 17) Dispersion comprising
- (a) core/shell particles according to at least one of Claims 1 to 11
 - (b) at least one solvent or dispersion medium and
 - (c) optionally dispersion aids.
- 18) Dispersion according to Claim 17, characterised in that the dispersion comprises at least one dispersion aid, where the dispersion aids employed are preferably water-soluble, high-molecular-weight organic compounds containing polar groups, such as polyvinylpyrrolidone, copolymers of vinyl propionate or acetate and vinylpyrrolidone, par-

tially saponified copolymers of an acrylate and acrylonitrile, polyvinyl alcohols having different residual acetate contents, cellulose ethers, gelatine, block copolymers, modified starch, low-molecular-weight polymers containing carboxyl and/or sulfonyl groups, or mixtures of these substances, where the proportion of dispersion aid in the dispersion is preferably in the range from 0.01 to 10% by weight, particularly preferably in the range from 0.5 to 5% by weight.

19) Dispersion according to at least one of the preceding claims, characterised in that the dispersion comprises at least one protective colloid, where the protective colloid employed is preferably polyvinyl alcohols having a residual acetate content of less than 35% by weight, in particular from 5 to 39 mol%, and/or vinylpyrrolidone-vinyl propionate copolymers having a vinyl ester content of less than 35% by weight, in particular from 5 to 30% by weight.

20) Dispersion according to at least one of the preceding claims, characterised in that the dispersion comprises at least one nonionic or ionic emulsifier, where the emulsifier employed is preferably ethoxylated or propoxylated, relatively long-chain alkanols or alkylphenols having different degrees of ethoxylation or propoxylation (for example adducts with from 0 to 50 mol of alkylene oxide) or neutralised, sulfated, sulfonated or phosphated derivatives thereof, in particular neutralised dialkylsulfosuccinic acid esters or alkylidiphenyl oxide disulfonates, where the use of nonionic emulsifiers and in particular the use of ethoxylated alkylphenols is preferred.

21) Dispersion according to at least one of the preceding claims, characterised in that the dispersion comprises at least one nonionic or ionic emulsifier and at least one protective colloid.

22) Process for the preparation of dispersions according to at least one of Claims 17 to 21 by

- a) surface treatment of dispersed monodisperse cores,
- b) application of the shell comprising organic polymers to the treated cores from a).

23) Process for the preparation of dispersions according to Claim 22, characterised in that the monodisperse cores are obtained by emulsion polymerisation in a step a1), and a crosslinked polymeric inter-layer, which preferably has reactive centres to which the shell can be covalently bonded, is applied to the cores, preferably by emulsion polymerisation or by ATR polymerisation, in a step a2).

24) Process for the preparation of dispersions according to at least one of the preceding claims, characterised in that step b) is a grafting, preferably by emulsion polymerisation or ATR polymerisation.

25) Process for the preparation of dispersions according to at least one of Claims 22 or 23, characterised in that the inorganic core is subjected to pre-treatment which enables bonding of the shell before the shell is polymerised on.

26) Process for the preparation of granules comprising core/shell particles, characterised in that a dispersion according to at least one of Claims 22 to 25 is dried and compounded.