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(54) Title: CORE-SHELL PARTICLES WITH ENCAPSULATED BROAD SPECTRUM ABSORBER CONTRAST AGENT

(57) Abstract: The present invention related to novel core-shell particles which comprise a broad spectrum absorber contrast agent and/or a precursors of a broad spectrum absorber contrast agent, as well as to the use of such core-shell particles and to the production of these core-shell particles.

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Core-shell particles with encapsulated broad spectrum absorber contrast agent

The present invention relates to novel core-shell particles which comprise a broad spectrum absorber contrast agent and/or precursors of a broad spectrum absorber contrast agent, as well as to the use of such core-shell particles and to the production of these core-shell particles.

Core shell particles are known from many patents as well as non-patent literature. For example from EP955323, EP1727839 and WO03/052035.
The core-shell particles disclosed in these patent applications are used in many fields of applications.

Surprisingly it has been found that due to the encapsulation of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent into the core-shell particles, the optical properties of colloidal crystals formed from core-shell particles according to the present invention are improved.

Therefore the present invention relates to core-shell particles wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particles.

This invention further relates to the process of production of the novel core-shell particles.

This invention further relates to the use of these particles in colourant compositions.

Furthermore the present invention finally relates to the use of these colourant compositions for coating or printing substrates as well as to material coated and/or printed by a colourant according to the present invention.

The core-shell particles according to the present invention must fulfill an important requirement: The difference Δn, which is the refraction index difference between the core material and the shell material is at least 0.001, preferably at least 0.01, especially at least 0.1.

The refraction index n of a medium is defined is defined as the ratio of the phase velocity of a wave phenomenon such as light or sound in a reference medium (usually vacuum) to the velocity in the medium itself. It is usually given the symbol n.

The core material can have the higher refractive index and the shell the lower, or vice versa, preferably the former.

By the term “encapsulated” we mean that the broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent is enclosed or embedded within the monodisperse particles. The broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent is (more or less) evenly distributed in the monodisperse particles. That means that it is not concentrated mainly in one part of the monodisperse particles.

In the light of the present invention the term “broad spectrum absorber contrast agent” also comprises a mixture of compounds wherein that mixture has the same absorption property as a single broad spectrum absorber contrast agent. Such a mixture still must eliminate diffuse light. That means that each single compound of such a mixture only absorbs the light in a well defined area and only the combination of these compounds provide a broad spectrum absorber.

In the following the term “broad spectrum absorber contrast agent” always stands for either a single compound or a mixture of compounds.

It is also possible to use a precursor of a broad spectrum absorber contrast agent. That precursor is converted into the broad spectrum absorber contrast agent by using a form of energy (such as light (UV), heat, etc). That means that the precursor can be transformed during the production of the inverse colloidal crystal or after its production.

Core-shell particles according the present invention can be such particles, wherein the broad spectrum absorber contrast agent and/or the precursor material of a broad spectrum absorber contrast agent is encapsulated in the core part of the core-shell particle.

Core-shell particles according the present invention can be such particles, wherein the broad spectrum absorber contrast agent and/or the precursor material of a broad spectrum absorber contrast agent is encapsulated in the shell part of the core-shell particle.

Core-shell particles according the present invention can be such particles, wherein the broad spectrum absorber contrast agent and/or the precursor material of a broad spectrum absorber contrast agent is encapsulated in the core part and in the shell part of the core-shell particle.

Suitable broad spectrum absorber contrast agents include absorbing elements such as silver, dyes such as Alizarin Blue Black and Brilliant Blue Black, as well as pigments and pigments such as carbon black (for example the carbon black product line from Degussa, such as Purex® LS 35 and Corax® N 115) and iron oxide black as well as other black metal oxides, such as silver oxide and iron hydroxide.

Suitable precursors for the present invention are metal salts, preferably hydrophilic metal salts, such as nitrates or halogenides. Preferred halogenides are F, Cl or I, whereas Cl is the most preferred halogenide.
The metals are for example alkaline metals, alkaline earth metals, noble metals, rare earth metals or transition metals. Suitable metals are for example K, Ca, Sr, Ba, Zn, Pb, Fe, Ni, Ce, Co, Cr, Cu, Mn, Sn, Al, Ag, Mg, Au, and Cd. Preferred are Ca. Mg, Al, Ag and Zn.
Very suitable metal salts are Ag nitrate, Ag halogenide, Fe nitrate and Fe halogenide (especially $FeCl_2$ and $FeCl_3$).

As an example $AgNO_3$ is converted into colloidal silver. It is also possible to use more than one precursor.
As a further example $FeCl_2$ as well as $FeCl_3$ are converted into black iron oxide and/or iron hydroxide.
Additionally it is also possible to use one or more precursor and another compound which form then a mixture, which has the required broad spectrum absorber contrast agent property. In the following the term “precursor of a broad spectrum absorber contrast agent” always stands for either a single compound or a mixture of compounds.

By this we mean that, as a pure material, the broad spectrum absorber contrast agent absorbs sufficient light so as to appear black or darkly coloured (for example dark blue or dark purple) to the human eye. For example, a broad spectrum absorber contrast agent absorbs most (particularly all) light having a wavelength in a range of from 380 to 780 nm. More specifically, the broad spectrum absorber contrast agent absorbs at least 90% (preferably at least 95%, more preferably 100%) of light having a wavelength in a range of from 380 to 780 nm.

The term “broad spectrum absorber contrast agent” is not intended to encompass those agents that do not absorb substantially all light having a wavelength in a range that corresponds to the wavelength of visible light (and, therefore, that, as a pure material, do not appear black or darkly coloured to the human eye). This term also is not intended to encompass single fluorescent agents, such as single fluorescent dyes or single pigments. But it is possible to encapsulate for example a mixture of various pigments, which have different absorption maxima and wherein the addition of these maxima has a broad spectrum absorber property.

The broad spectrum absorber contrast agent can be organic, that means that it comprises atoms selected from carbon, hydrogen, oxygen, nitrogen and/or sulfur only.
The broad spectrum absorber contrast agent can be inorganic, that means that it comprises metal atoms.
Inorganic broad spectrum absorber contrast agents are preferred.

In the compositions of the present invention, the broad spectrum absorber contrast agent typically absorbs substantially all of the light that is diffused by the colloidal inverse crystal and that has a wavelength in a range that corresponds to the wavelength of visible light. Contrast agents that are not broad spectrum absorbers as defined herein do not absorb substantially all of the diffused light. The unabsorbed, diffused light dilutes the structural colour effect caused by the direct reflection and/or diffraction of visible light by the inverse crystal.

The broad spectrum absorber contrast agent may, for example, be a dye or a pigment or a mixture of dyes or a mixture of pigments and dyes as well as a mixture of pigments and dyes, which fulfils the requirements for the broad spectrum absorber contrast agent as defined in the present patent application. A “dye” generally has an affinity to the substrate to which it is applied and generally is in the form of a solution or an oil. A “pigment” generally does not have an affinity to the substrate to which it is applied and is in the form of a solid. As the skilled person would appreciate, the exact physical form of the contrast agent is not essential to the present invention and the physical form may change upon application of the colourant composition to a suitable substrate.

The core-shell particles according to present invention are monodisperse.

By the term “monodisperse particles” we mean particles wherein at least 60% of the particles fall within a specified particle size range. For example, the monodisperse particles preferably have a diameter that deviates less than 10% in root mean square (rms), more preferably that deviates less than 5% in rms diameter, especially preferably even less than 3% in rms diameter.

The particle size distribution can be determined in a conventional manner, for example by means of an analytical ultracentrifuge (see for example W. Machtle, Makromol. Chem. 185 (1984), p. 1025-1039)

The materials of core and shell can be inorganic, organic, metallic or hybrid materials, provided they meet the above-specified conditions.

However, with regard to the desirability of being able to vary relevant properties of the cores of the core-shell particles of the invention as required, it is advantageous for the cores to comprise or consist of one or more polymers and/or copolymers (core polymers).

The use of polymeric substances as core and shell material gives the person skilled in the art the freedom to define their relevant properties, for example their composition, the particle size, the mechanical data, the refractive index, the glass transition temperature, the melting point and the weight ratio of core:shell and hence also the application properties of the core-shell particles, which ultimately also affect the properties of the effect colorants produced therefrom.

The cores preferably comprise a single polymer or copolymer. For the same reason, it is advantageous for the shell of the core-shell particles of the invention likewise to comprise one or more polymers and/or copolymers (shell polymers; matrix polymers) or polymer precursors and optionally auxiliary and additive substances, the shell composition being choosable in such a way that the shell, when in a nonswelling environment at room temperature, is essentially form-stable and nontacky.

The cores of the core-shell particles of the invention have an essentially spherical, preferably globular, shape. In many cases, the cores within this structure form a close spherical packing.

The cores of the core-shell particles of the invention have a size within the range from 50 to 700 nm, preferably within the range from 50 to 500 nm, especially within the range from 50 to 400 nm. They have a monodisperse distribution, i.e., are present in a narrow particle size distribution.

Polymers and/or copolymers making up the core material in whole or in part are high molecular weight compounds. Suitable polymers and copolymers include not only addition polymers and copolymers of polymerizable unsaturated monomers, but also poly-condensates and copolycondensates of monomers having two or more reactive groups, e.g., high molecular weight aliphatic, aliphatic/aromatic or wholly aromatic polyesters, polyamides, polycarbonates, polyureas and polyurethanes, but also amino and phenolic resins, for example melamine-formaldehyde, urea-formalde-hyde and phenol-formaldehyde condensates.

The polymers of the core material can be crosslinked (co)polymers. They also promote the formation of core-shell structures when the core-shell particles of the invention are being prepared. These crosslinked polymers can either have already been cross-linked in the course of the addition (co)polymerization or (co)polycondensation, or have been aftercrosslinked in a separate step following the actual addition (co)polymerization or (co)polycondensation.

A detailed description of the chemical composition of suitable polymers follows later hereinbelow. Additionally a list of suitable polymers for the core can be found in WO03/058299 (Table 1, on page 5 to 10).

A further embodiment of the present invention relates to core-shell particles, wherein the core of the particles is essentially form-stable. Form-stable means that the cores of the particles keep their shape and size during the usual use or usual application of the particles.

To confer a very wide application spectrum on the core-shell particles of the invention, it is advantageous for the shell material likewise to comprise or consist of one or more polymers and/or copolymers. It is preferable, especially for economic reasons, for the shell material to comprise or consist of one polymer.

Useful polymers for the shell material are in principle, as for the core material, polymers of the classes mentioned above, provided they are selected or constructed in such a way that they meet the specification given above for the shell polymers.

Accordingly, they have to have a refractive index which differs distinctly from that of the core polymers, i.e., low refractive shell polymers have to be used with high refractive core polymers, and vice versa. Furthermore, they should not tend to swell or dissolve the cores.

The shell of the core-shell particles according to the present invention can be formed from formstable material as well as from a non-formstable, e.g. filmable material.
The core-shell particles according to the present invention can also have more than shell layer, whereas each of these layers can be formstable or non-formstable.
Therefore a further embodiment of the present invention are core-shell particles comprising more than one shell layer.
When the shell material is non-formstable, a matrix system is built up by the shells of the particles. The result of such a process is that the shells of the particles are merged. The cores of the core-shell particles are (essentially) still at the same spot.

In case the shell material is non-formstable, the shell polymers can either be softenable or liquefiable by simple measures by undecomposed melting--if necessary with the assistance of auxiliary and/or additive substances present in the shell or separately added to the core-shell particle powders prior to use--or producible from polymer precursors (prepolymers, monomers) which are part of a softenable or liquefiable shell material. The softening or liquefication, as explained above, shall be sufficient for the cores of the core-shell particles to be able to form at least domains of regular order.

Prepolymers for the purposes of this invention are polymers having a low or medium degree of polymerization which can be converted into the desired polymers by further condensation or crosslinking. The shell and/or the core part of the core-shell particle according to the present invention can be crosslinked.

This crosslinking can be effected via the same polyfunctional monomers as in the case of the core polymers, taking, account of the required refractive index differences.

The crosslinker substances can be part of the shell material, they can be separately added to the core-shell particle prior to its use, i.e., prior to filming, or they can be applied subsequently, after filming, (postcrosslinking).

It is favorable for certain applications, as for the production of coatings or colored films, for the polymer material of the shell of the core-shell particles of the invention which forms the matrix phase to be an elastically deformable polymer, for example an addition polymer having a low glass transition temperature.

In this case, the color of a layer of the colorant of the invention can be made to vary in response to elongation and compression.

Polymers which meet the specifications for a matrix material are likewise members of the groups of the addition polymers and copolymers of polymerizable unsaturated monomers and also of the polycondensates and copolycondensates of monomers having two or more reactive groups, e.g., high molecular weight aliphatic, aliphatic-aromatic or wholly aromatic polyesters and polyamides, but also of the amino and phenolic resins, such as melamine-formaldehyde, urea-formaldehyde and phenol-formaldehyde condensates, which dry with further condensation and considerable crosslinking. The same applies to epoxy resins, consisting, for example, of mixtures of polyepoxies and polyamines or polyols, which dry to solid resinous materials.

Epoxy resins are typically prepared by mixing epoxy prepolymers, obtained for example by reaction of bisphenol A or other bisphenols, resorcinol, hydroquinone, hexanediol or other aromatic or aliphatic di- or polyols or phenol-formaldehyde condensates or mixtures thereof with epichlorohydrin, dicyclopentadiene diepoxide or other di- or polyepoxies, with further condensation-capable compounds directly or in solution and allowing the mixture to cure.

With regard to the above conditions of the properties of shell (=matrix) polymers, selected building blocks from all groups of organic film-formers are in principle suitable for their preparation.

Shell polymers which are soluble, or at least well swellable, in organic solvents and which therefore are used with advantage as film-formers for matrices which bind by drying on are, for example, modified or moderately high molecular weight polyesters, cellulose esters such as cellulose acetobutyrate, polyurethanes, silicones, polyether or polyester-modified silicones.

A further embodiment of the present invention are core-shell particles wherein the shell material be filmable, i.e., that it may by simple measures be softened, viscoelasticized or liquefied to such an extent that the cores of the core-shell particles are able to form at least domains of regular order. The filmed shell material then forms (depending on its mass fraction in the core-shell particles) either a continuous phase which fills out all interstitial spaces between the core particles, a matrix, or adhesive dots in the region of the contact points between the core particles, which adhesive dots fix the core particles in a regular arrangement. (The shell material may therefore also be referred to under the synonyms of matrix material or matrix phase.) The cores arrayed in a regular order in the matrix formed by the filming of the shell of the core-shell particles form a diffraction grating which creates interference phenomena and thereby leads to very interesting color effects.

The shell material may include auxiliary and/or additive substances in a proportion of up to 40% by weight, preferably up to 20% by weight, especially within the range from 5 to 20% by weight, of the shell weight.

The core-shell particles of the invention have a size within the range from 55 to 900 nm, preferably within the range from 55 to 600 nm, especially within the range from 55 to 500 nm. They have a monodisperse distribution, i.e., are present in a narrow particle size distribution.

The ratio between the core part and the shell part of the core-shell particle can vary a lot. Usually the ratio of core:shell goes from 1:100 to 100:1, preferably 1:10 to 50 :1, more preferably 1:3 to 25:1.
A very preferred ratio is 1:1.

The core shell particles can comprise up to 3 weight-% (wt-%), based on the total weight of the core-shell particles, of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent, which is encapsulated in the core-shell particles.

The goal of the present invention is not to produce coloured particles, but to produce colourless particles, wherein a colour effect is achieved by colloidal crystal arrangement. Therefore the amount of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent encapsulated in such monodisperse particles must not be too high (less than 3 wt-%, based on the total weight of the monodisperse particles). The amount varies depending on the absorption coefficient of the broad spectrum absorber contrast agent and/or the precursor of a broad spectrum absorber contrast agent.

Usually the core-shell particles comprise 0.0001 wt-% - 3wt-%, based on the total weight of the core-shell particles, of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent, which is encapsulated in the core-shell particles.
The broad spectrum absorber contrast agent and/or the precursor of a broad spectrum absorber contrast agent can be in the core part and/or in the shell part of the core-shell particle.

Preferably, the core-shell particles comprise 0.0001 wt-% - 1wt-%, more preferably 0.0001 – 0.5wt-% based on the total weight of the core-shell particles, of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent, which is encapsulated in the core-shell particles.

Usually, the core-shell particles which contain the encapsulated broad spectrum absorber contrast agent comprise

(i) 97 – 99.9999 weight-% (wt-%), preferably 99 – 99.9999 wt-%, more preferably 99.5 – 99.9999 wt-%, based on the total weight of the core-shell particles, of the shell-particle material, and

(ii) 0.0001 – 3 wt-%, preferably 0.0001 – 1 wt-%, more preferably 0.0001 – 0.5 wt-%, based on the total weight of the core-shell particles, of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent, which is encapsulated in the core-shell particles.

It is obvious that the addition of the wt-% of (i) and of (ii) is 100%.

Processes for producing core shell particles are well known in the prior art. For examples from WO03/25035, EP955323 or WO05/056622.
For obtaining the new core shell particles according to the present invention it is necessary to add at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent during the production of the core and/or to the production of the shell.

The core/shell particles according to the invention can be produced by various processes. A preferred way of obtaining the particles is a further subject-matter of the present invention. This is a process for the production of core/shell particles by a) surface treatment of monodisperse cores, and b) application of the shell of organic polymers to the treated cores., wherein tat least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent is present in step a) and/or step b).

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

In a preferred variant of the invention, a crosslinked polymeric interlayer, which preferably contains reactive centres to which the shell can be covalently bonded, is applied to the cores in step a), preferably by emulsion polymerisation or by ATR polymerisation. ATR polymerisation here stands for atom transfer radical polymerisation, as described, for example, in K. Matjaszewski, Practical Atom Transfer Radical Polymerisation, 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 Polymerisation from Nanoparticles: A Tool for the Preparation of Well-Defined Hybrid Nanostructures and for Understanding the Chemistry of Controlled/"Living" Radical Polymerisation 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.

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 at between 20 and 80°C. Particularly preferred polymerisation initiators are peroxides, such as dibenzoyl peroxide, di-tertbutyl 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 production of polycondensation products. Thus, it is possible for the starting materials for the production 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 or hydroxyamines. Like the polycondensations, 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 produced using dispersion auxiliaries

The dispersion auxiliaries used are preferably water-soluble, high-molecular-weight organic compounds having 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, gelatin, block copolymers, modified starch, low-molecular-weight polymers containing carboxyl and/or sulfonyl groups, or mixtures of these substances.

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 optionally 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. Neutralised dialkylsulfosuccinic acid esters or alkyldiphenyl oxide disulfonates are also particularly suitable.

Particularly advantageous are combinations of these emulsifiers with the above-mentioned protective colloids, since particularly finely divided dispersions are obtained therewith.

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 production--in terms of type and proportion--the desired property combinations of the requisite polymers can be set specifically. The particle size here can be set, for example, through the choice and amount of the initiators and other parameters, such as the reaction temperature. The corresponding setting of these parameters does not present any difficulties at all to the person skilled in the art in the area of polymerisation.

Monomers which result in polymers having a high refractive index are generally those which contain aromatic moieties or those which contain heteroatoms having a high atomic number, such as, for example, those halogen atoms, in particular bromine or iodine atoms, sulfur or metal ions, i.e. atoms or atomic groups which increase the polarisability of the polymers.

Polymers having a low refractive index are accordingly obtained from monomers or monomer mixtures which do not contain the said moieties and/or atoms of high atomic number or only do so in a small proportion.

The core-shell particles obtained can be isolated in a conventional manner, for example by removing the liquid reaction medium. The core-shell particles thus prepared generally form aggregates (microscopic particles possessing high spherical symmetry, in the case of spray drying) on whose surface a surprisingly regular, crystal lattice type array of the core-shell particles of the invention is observable.

By removing the liquid reaction medium it is possible to isolate the core-shell particles or preparations comprising auxiliary and/or additive substances. Depending on the nature and the amount of the auxiliary and/or additive substances added, this provides solid, pasty or liquid preparations.

The reaction mixtures obtained on completion or discontinuation of the polymerization reaction can also be further processed directly, i.e., without isolation of the core-shell particles. They then represent preparations which, as auxiliary and/or additive substances, merely include the emulsifiers used and the liquid reaction medium. If desired, partial removal of the reaction medium is also possible to increase the core-shell particle content of the preparation if required.

The core polymer particles to be provided in the above-described process for preparing the core-shell particles of the invention can be prefabricated in a separate polymerization process.

However, it is particularly economical for the process to be carried out in a two-step one-pot process, the core polymer particles being prepared from the selected polymer precursors (monomers and/or prepolymers) in the first reaction step and subsequently, without isolation of the core particles, the batch being admixed with the polymer precursors required for shell formation, and optionally with auxiliary and additive substances, and then being further processed as described above.

To specifically produce solid preparations, the polymerization of the shell polymers is carried out in the presence of all or some of the auxiliary and/or additive substances present in the preparation and optionally dispersion or diluent media, or these are wholly or partly added during or after the polymerization, in which case the adds are chosen so that their mixture is solid, and the inert reaction medium is removed on completion of the polymerization.

In the production of the core-shell particles of the invention and their preparations, the inert reaction medium is preferably removed by freeze drying or by spray drying or, in the case of previously applied preparations, by evaporation under reduced pressure.

The preparation of the addition polymers for core and shell is not restricted to a specific process. On the contrary, existing polymermaking processes can be used. It is preferable to use the processes of emulsion polymerization, suspension polymerization, microemulsion polymerization or microsuspension polymerization which employ free-radical addition polymerization. They offer the advantage of not being sensitive to moisture.

The core-shell particles as described above can be used in colourant compositions.

The colourant compositions of the present invention comprising core-shell particles as described above may be applied to any suitable substrate to colour at least a region of the substrate.

The colouring composition of the present invention can be used to print on and/or to coat any commonly known substrates.
Suitable substrates for printing and coating include fibre (such as hair), skin, nails, food material, stone, ceramic, glass, paper, fabrics, wood, leather, metal (for example aluminium) and plastics.

Therefore an embodiment of the present invention is a colorant composition (CC 1) comprising

(a) core-shell particles as described above, wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that
at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particle.

The colouring composition can also comprise core-shell particles, which comprise no broad spectrum absorber contrast agent and/or precursor of a broad spectrum absorber contrast agent.

A further embodiment of the present invention is a colorant composition (CC 2) comprising

(a) core-shell particles as described above, wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that
at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particles and

(b) core-shell particles wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that
no broad spectrum absorber contrast agent and no precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particle.

It is clear that in such a colourant composition which comprises a mixture of core-shell particles, core-shell particles which comprise no broad spectrum absorber contrast agent and no precursor of a broad spectrum absorber contrast agent can be produced in the same way as the core-shell particles comprising at least one broad spectrum absorber contrast agent.

The colourant compositions of the present invention may typically be in liquid form; semi-liquid form including lotions, pastes, creams, mousses, waxes ; or solid form including powders for example laundry powders or tablets.

The colourant composition according to the present invention comprise from 0.01 wt-% to 70 wt-%, based on the total weight of the colouring composition, of the core-shell particles.

In case that the coloring composition is in solid form it also possible that the coloring composition comprises up to 100 wt-%, based on the total weight of the coloring composition, of the core-shell particles as described above.

A further embodiment of the present invention relates to a colourant composition (CC 3) comprising

(a) 0.01 wt-% to 70 wt-%, based on the total weight of the colourant composition, of core-shell particles as described above, wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that
at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particles.

When the colourant composition is in the form of a liquid, gel or paste, then the composition comprises at least one solvent.

A further embodiment of the present invention relates to a colourant composition (CC 4) comprising

(a) core-shell particles as described above, wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particles, and

(b) at least one solvent.

Preferably the solvent is an organic solvent, which can be polar or nonpolar. Examples of polar solvents include water, alcohols (mono or poly), esters, ketones and ethers, particularly mono- and di-alkyl ethers of glycols and polyglycols such as monomethyl ethers of mono-, di- and tri-propylene glycols and the mono-n-butyl ethers of ethylene, diethylene and triethylene glycols.

Examples of nonpolar solvents include aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

The colourant composition can be prepared as an aqueous or as a nonaqueous solution.

Therefore, another embodiment of the present invention relates to a colourant composition as described above, wherein the formulation is nonaqueous.

Therefore, another embodiment of the present invention relates to a colourant composition as described above, wherein the formulation is aqueous.

A further embodiment of the present invention relates to a colourant composition (CC 5) comprising

(a) of core-shell particles as described above, wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particles, and

(b1) water, and

(b2) optionally at least one solvent, chosen from the group consisting of alcohols, esters, ketones, ethers and aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

A further embodiment of the present invention relates to a colourant composition (CC 6) comprising

(a) of core-shell particles as described above, wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particles, and

(b1) water, and

(b2) optionally at least one solvent, chosen from the group consisting of alcohols, esters, ketones, ethers and aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

Therefore, the present invention also relates to a colourant composition (CC 7) comprising

(a) of core-shell particles as described above, wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particles, and

(b) at least one solvent, chosen from the group consisting of alcohols, esters, ketones, ethers and aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

A further embodiment of the present invention relates to a colourant composition (CC 8) comprising

(a) of core-shell particles as described above, wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particles, and

(b) at least one solvent, chosen from the group consisting of alcohols, esters, ketones, ethers and aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

But, even when no water is deliberately added to the nonaqueous composition, some adventitious water may be carried into the composition, but generally this will be no more than about 2 wt-% – 4 wt-%, based on the total weight of colourant composition. By definition, the nonaqueous composition of this invention will have no more than about 4 wt-%, and preferably no more than about 2 wt-% water based on the total weight of colourant composition.

The amount of solvent in a colourant composition according to the present invention is typically in the range of about 10 wt-% to about 99.99 wt-%, preferably from about 20 wt-% to about 99.9 wt-%, and more preferably from about 30 wt-% to about 99.9 wt-%, based on total weight of the colourant composition.

The amount of solvent, which is part of the inventive formulation, can vary a lot.
When the composition is used as a concentrate, which is to be diluted (with water and/or other solvents), then the amount of solvents is low, usually between 30 wt-% and 70 wt-%, based on the total weight of the colourant composition. In certain cases the colouring composition can comprise even less that 30 wt-% of solvents.
When the formulation is in a “ready-to-use”-form then the solvent content can be up to 99.5 wt-%, based on the total weight of the colourant composition.

It is obvious that the amount of solvent also depends on the substrate which is to be coated or printed as well as on the hue which needs to be obtained.

Therefore, the present invention also relates to a concentrated colourant composition, wherein the amount of solvent lies between 30 wt-% and 70 wt-%, preferably between 40 wt-% and 70 wt-%, more preferably between 50 wt-% and 70 wt-%, based on the total weight of colourant composition.

The present invention also relates to a colourant composition, wherein the amount of water lies between 70 wt-% and 99.99 wt-%, -%, preferably between 70 wt-% and 99.9wt-%, more preferably between 80 wt-% and 99.9 wt-%, based on the total weight of the colourant composition.

It also to be stated that the amount of the core-shell particles as well as of the solvent can vary depending of the physical form of the composition, that means the concentration can vary in case the colourant composition is a solid, liquid, gel, mousse, wax or a paste.

It is also possible to add monodisperse core-shell particles which do not comprise any broad spectrum absorber contrast agent and do not comprise any broad spectrum absorber contrast agent. It is clear that these core-shell particles should have the same dimension as the core-shell particles comprising the absorber. Otherwise, the colour effect will be detoriated.

A further embodiment of the present invention relates to a colourant composition (CC 9) comprising

(a) 0.01 wt-% to 70 wt-%, based on the total weight of the colourant composition, of core-shell particles as described above, wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that
at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particles, and

(b) 30 wt-% and 99.99 wt-%, based on the total weight of the colourant composition, of at least one solvent.

A further embodiment of the present invention relates to a colourant composition (CC 10) comprising

(a) 0.01 wt-% to 70 wt-%, based on the total weight of the colourant composition, of core-shell particles, which comprise

    97 to 99.9999 wt-% (preferably 99 to 99.999 wt-%, more preferably 99.5 to 99.9999 wt-%), based on the total weight of core-shell particles, of core material and shell material and

0.0001 to 3 wt-% (preferably 0.0001 to 1 wt-%, more preferably 0.0001 to 0.5 wt-%), based on the total weight of the core-shell particles, of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent chosen from the group consisting of Alizarin Blue Black, Brilliant Blue Black, carbon black, black iron oxide, iron hydroxide, iron oxide black, silver oxide black K, Ca, Sr, Ba, Zn, Pb, Fe, Ni, Ce, Co, Cr, Cu, Mn, Sn, Al, Ag, Mg, Au, Cd, Ag nitrate, Ag halogenide, Fe nitrate and Fe halogenide,

(b1) 30 wt-% and 99.99 wt-%, based on the total weight of the colourant composition, of water, and

(b2) optionally 0.1 wt-% and 89.99 wt-%, based on the total weight of the colourant composition, of at least one solvent, chosen from the group consisting of alcohols, esters, ketones, ethers and aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

A further embodiment of the present invention relates to a colourant composition (CC 11) comprising

(a) 0.01 wt-% to 70 wt-%, based on the total weight of the colourant composition, of core-shell particles, comprising

97 to 99.9999 wt-% (preferably 99 to 99.999 wt-%, more preferably 99.5 to 99.9999 wt-%), based on the total weight of core shell particles, of core material and shell material and

0.0001 to 3 wt-% (preferably 0.0001 to 1 wt-%, more preferably 0.0001 to 0.5 wt-%), based on the total weight of the core-shell particles, of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent chosen from the group consisting of Alizarin Blue Black, Brilliant Blue Black, carbon black, black iron oxide, iron hydroxide, iron oxide black, silver oxide black, K, Ca, Sr, Ba, Zn, Pb, Fe, Ni, Ce, Co, Cr, Cu, Mn, Sn, Al, Ag, Mg, Au, Cd, Ag nitrate, Ag halogenide, Fe nitrate and Fe halogenide,

(b) 30 wt-% and 99.99 wt-%, based on the total weight of the colourant composition, of at least one solvent, chosen from the group consisting of alcohols, esters, ketones, ethers and aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

A further embodiment of the present invention relates to a colourant composition (CC 12) comprising

(a) 0.01 wt-% to 70 wt-%, based on the total weight of the colourant composition, of core shell particles, comprising

97 to 99.9999 wt-% (preferably 99 to 99.999 wt-%, more preferably 99.5 to 99.9999 wt-%), based on the total weight of core shell particles, of core material and shell material and

0.0001 to 3 wt-% (preferably 0.0001 to 1 wt-%, more preferably 0.0001 to 0.5 wt-%), based on the total weight of the core-shell particles, of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent chosen from the group consisting of Alizarin Blue Black, Brilliant Blue Black, carbon black, black iron oxide, iron hydroxide, iron oxide black, silver oxide black, K, Ca, Sr, Ba, Zn, Pb, Fe, Ni, Ce, Co, Cr, Cu, Mn, Sn, Al, Ag, Mg, Au, Cd, Ag nitrate, Ag halogenide, Fe nitrate and Fe halogenide,

(b1) 30 wt-% and 99.99 wt-%, based on the total weight of the colourant composition, of water, and

(b2) optionally 0.1 wt-% and 89.99 wt-%, based on the total weight of the colourant composition, of at least one solvent, chosen from the group consisting of alcohols, esters, ketones, ethers and aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

A further embodiment of the present invention relates to a colourant composition (CC 13) comprising

(a) 0.01 wt-% to 70 wt-%, based on the total weight of the colourant composition, of core-shell particles, comprising

97 to 99.9999 wt-% (preferably 99 to 99.999 wt-%, more preferably 99.5 to 99.9999 wt-%), based on the total weight of core shell particles, of core material and shell material and

0.0001 to 3 wt-% (preferably 0.0001 to 1 wt-%, more preferably 0.0001 to 0.5 wt-%), based on the total weight of the core-shell particles, of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent chosen from the group consisting of Alizarin Blue Black, Brilliant Blue Black, carbon black, black iron oxide, iron hydroxide, iron oxide black, silver oxide black, K, Ca, Sr, Ba, Zn, Pb, Fe, Ni, Ce, Co, Cr, Cu, Mn, Sn, Al, Ag, Mg, Au, Cd, Ag nitrate, Ag halogenide, Fe nitrate and Fe halogenide,

(b) 30 wt-% and 99.99 wt-%, based on the total weight of the colourant composition, of at least one solvent, chosen from the group consisting of alcohols, esters, ketones, ethers and aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

A further embodiment of the present invention also relates to a colourant composition (CC 14) formulation which additionally comprises

(c) at least one curing material, and

(d) at least one initiator.

The colourant composition (CC 1), (CC 2), (CC 3), (CC 4), (CC 5), (CC 6), (CC 7), (CC 8), (CC 9), (CC 10), (CC 11), (CC 12) and/or (CC 13) according to the present invention can also comprises at least one curing agent and at least one initiator.
Any kind of commonly known curing agents can be used.
Usually, curing agents are resins which are crosslinkable. These are low molecular or oligomeric polyfunctional compounds with a molecular mass <1000 g/mol. The functional groups which are often terminal groups (for example epoxy-, isocyanate-, amine- or hydroxy-groups) are chosen that way (amount of groups as well as kind of the groups) that they react according to the polyaddition- or polycondensation-mechanism.
Suitable curing agents are epoxy acrylates, polyurethane acrylates, polyester acrylates, acrylated polyols and acrylated polyethers.
Such curing agents are used in an amount of 0.01wt-% - 15wt-%, based on the total weight of the colourant composition. Preferably, curing agents are present in an amount of 0.1 – 10 wt-%, based on the total weight of the colourant composition.

In combination with the curing agent at least one initiator is used, which starts the polyaddition or polycondensation of the curing agent. This is usually done by light (400 nm - 800nm) or UV-light (100 nm – 400 nm)
Such an initiator can be peroxide or peroxide containing compounds, benzophenone and benzophenone derivatives, acetophenone and acetophenone derivatives, benzoin ether derivatives or thioxanthones derivatives.

Such initiators are used in an amount of 0.005wt-% - 10wt-%, based on the total weight of the colourant composition. Preferably, initiators are present in an amount of 0.01 – 8 wt-%, based on the total weight of the colourant composition.

A further embodiment of the present invention relates to a colourant composition (CC 15), which additionally comprises

(c) 0.01 wt-% to 15wt-%, based on the total weight of the colourant composition, of at least one curing material, and

(d) 0.005wt-% to 10wt-%, based on the total weight of the colourant composition, of at least one initiator.

A further embodiment of the present invention relates to a colourant composition (CC 16), which additionally comprises

(c) 0.01 wt-% to 15wt-%, based on the total weight of the colourant composition, of at least one curing material chosen from the group consisting of epoxy acrylates, polyurethane acrylates, polyester acrylates, acrylated polyols and acrylated polyethers,

(d) 0.005wt-% to 10wt-%, based on the total weight of the colourant composition, of at least one initiator chosen from the group consisting of peroxide or peroxide containing compounds, benzophenone and benzophenone derivatives, acetophenone and acetophenone derivatives, benzoin ether derivatives and thioxanthones derivatives.

All the preferences for the curing agent and the initiator in regard to the compounds as well as the concentrations can be applied to the colourant compositions (CC 1), (CC 2), (CC 3), (CC 4), (CC 5), (CC 6), (CC 7), (CC 8), (CC 9), (CC 10), (CC 11), (CC 12) and/or (CC 13) as described above as well.

Additionally the colouring composition (CC 1), (CC 2), (CC 3), (CC 4), (CC 5), (CC 6), (CC 7), (CC 8), (CC 9), (CC 10), (CC 11), (CC 12), (CC 13), (CC 14), (CC 15) and/or (CC 16) can comprise further auxiliaries. Such auxiliaries are these commonly used in the field of colouring, such as coating and printing.
Auxiliaries are those additional chemicals which are used to improve the results of the coating or printing process. Furthermore, under the term auxiliaries is to be understood the chemicals, which help to improve the property of the formulation itself, such as storage, better manipulability of the colourant composition, etc.

Examples of auxiliaries are wetting agents, buffer substances, antistatic agents, bleaching agents, oxidation agents, rheology modifiers, solubilizers, siccative, antifoams, levelling agents, surfactants, electrolytes, foam suppressants, antifreezing agents or fungistatic and/or bacteriostatic agents, optical brighteners, softeners, flameproofing additives, or dirt repellents, water repellents and oil repellents, as well as water softeners and natural or synthetic thickeners, e.g. alginates and cellulose ethers.

Such auxiliaries are usually present in a smaller amount, which can go up to about 10 wt-%, based on the total weight of the colourant composition.
If one or more auxiliaries are present the amount goes usually from 0.1 wt-% to 10 wt-%, based on the total weight of the colourant composition.

Therefore a further embodiment of the present invention relates to a colourant composition as described above comprising additionally at least one auxiliary.

Therefore a further embodiment of the present invention relates to a colourant composition (CC 17) additionally comprising

(e) at least one auxiliary.

Therefore a further embodiment of the present invention relates to a colourant composition (CC 18) additionally comprising

(e) at least one auxiliary chosen from the group consisting of wetting agents, buffer substances, antistatic agents, bleaching agents, oxidation agents, rheology modifiers, solubilizers, siccative, antifoams, levelling agents, surfactants, foam suppressants, antifreezing agents or fungistatic and/or bacteriostatic agents, optical brighteners, softeners, flameproofing additives, or dirt repellents, water repellents and oil repellents, as well as water softeners and natural or synthetic thickeners, e.g. alginates and cellulose ethers.

Another embodiment of the present invention relates to a colourant composition (CC 19) additionally comprising

(e) 0.1 wt-% to 10 wt-%, based on the total weight of the colourant composition, of at least one auxiliary.

Another embodiment of the present invention relates to a colourant composition

(CC 20) additionally comprising

(e) 0.1 wt-% to 10 wt-%, based on the total weight of the colourant composition, of at least one auxiliary from the group consisting of wetting agents, buffer substances, antistatic agents, bleaching agents, oxidation agents, rheology modifiers, solubilizers, siccative, antifoams, levelling agents, surfactants, foam suppressants, antifreezing agents or fungistatic and/or bacteriostatic agents, optical brighteners, softeners, flameproofing additives, or dirt repellents, water repellents and oil repellents, as well as water softeners and natural or synthetic thickeners, e.g. alginates and cellulose ethers.

All the preferences for the curing agent and the initiator in regard to the compounds as well as the concentrations can be applied to the colourant compositions (CC 1), (CC 2), (CC 3), (CC 4), (CC 5), (CC 6), (CC 7), (CC 8), (CC 9), (CC 10), (CC 11), (CC 12), (CC 13), (CC 14), (CC 15) and/or (CC 16) as described above as well.

As already mentioned the colourant compositions according to the present invention can be in any suitable physical form. Usually it is in the form of a solid, liquid, a gel, mousse, wax or a paste.

A further embodiment of the present invention relates to a colourant composition as described above, which is a coating and/or a printing formulation.

The printing process can be done according to any well known processes such as Ink jet (such as Bubble Jet, Compound jet, Dry Inkjet, Hotmelt Inkjet), relief printing, intaglio, letterpress, lithography, flexography, gravure, screen printing and pad printing. Therefore the formulations have to be adapted to the desired form of printing technology. Formulations for the inkjet technology comprising monodisperse particles are for example known from WO2005/063902.

Therefore a further embodiment of the present invention relates to a colourant composition which is a printing formulation for Ink jet (such as Bubble Jet, Compound jet, Dry Inkjet, Hotmelt Inkjet), relief printing, intaglio, letterpress, lithography, flexography, gravure, screen printing and pad printing.

The colourant composition as described in the present patent application can also be used for any known coating technology.

Therefore the formulations have to be adapted to the desired form of coating technology. Suitable coating processes are for example air knife coating, immersion (dip) coating, Gap Coating, Curtain coating, rotary screen, Reverse Roll coating, Gravure coating, Metering rod (Meyer bar) coating, Slot Die (Extrusion) coating and Hot Melt coating.

The colourant compositions according to the present invention can also be used in personal care formulations and cosmetic formulations.

Therefore a further embodiment of the present invention is the use of inverse colloidal crystals as described above and colourant compositions as described above in personal care formulations especially in cosmetic formulations.

Therefore a further embodiment of the present invention also relates to personal care formulations and/or cosmetic formulations comprising core-shell particles as described above and/or at least one colourant composition as described above.

The personal care formulations and/or cosmetic formulations can have any usual form of application. They can be in the form of, for example, solutions, suspensions, emulsions, PIT emulsions, pastes, ointments, gels, creams, lotions, powders, soaps, surfactant-containing cleansing preparations, oils, aerosols, mousses, waxes, sprays and sticks.
The personal care formulations especially the cosmetic formulations can be used for any personal care and/or cosmetic application. They can be used for example as lipsticks, lip-cares sticks, mascara, eyeliner, eye-shadow, rouge, powder make-up, emulsion make-up, wax make up, nail lacquer, shampoos and shower compositions.
The personal care formulations as well as the cosmetic formulations may comprise any commonly used ingredients and additives for a cosmetic use, such as solvents, further dyes and/or pigments, antioxidants, repellents, vitamins, UV-absorbers, solutes, self-tanning agents, preservatives, antioxidants, stabilisers, solubilisers, vitamins, colorants and odour improvers.

Preferred cosmetic compositions are those suitable for the application to human skin, which optionally, but preferably, include a skin benefit agent in addition to the colourant compositions of the present invention. Suitable additional skin benefit agents include anti-aging, wrinkle-reducing, skin whitening, anti-acne and sebum reduction agents. Examples of these include alpha-hydroxy acids, beta-hydroxy acids, polyhydroxy acids, hydroquinone, t-butyl hydroquinone, Vitamin B and C derivatives, dioic acids, retinoids; betulinic acid; vanillic acid; allantoin, a placenta extract; hydrolactin; and resorcinol derivatives.

Following a suitable contact time, excess composition can be removed/washed off if necessary. Preferably the cosmetic composition is in contact with the skin, nail or hair for sufficient time such that at least two or three colloidal crystalline layers are formed.

The concentration of the ingredients can vary a lot, but a person skilled in the art knows which concentration of a specific ingredient is necessary to produce the various application forms.
The new inverse colloidal crystals according to the present invention can be used in any known personal care formulations and cosmetic formulations. Suitable formulations can be found for example in US2006002875.

Therefore a further embodiment of the present invention is a personal care formulation comprising core-shell particles according to the present invention.

Therefore a further embodiment of the present invention is a cosmetic formulation comprising core-shell particles according to the present invention.

A further area of application for core-shell particles according to the present invention is the security sector with various applications, for example in bank notes, credit cards, visas, tax seals or the like.

Therefore a further embodiment of the present invention is a security printing and/or coating ink comprising core-shell particles according to the present invention.

Such an ink is used to produce security marking, thread or device, hologram, hot stamping foil or watermark, in particular for the purpose of prevention of counterfeiting, authentification, verification, or identification of data or information, comprising an optically variable marking as described above and below.

The security elements also comprise an additional detectable security feature, in particular an optically, machine or haptically detectable security feature.

Therefore a further embodiment of the present invention is a security printing and/or coating ink comprising core-shell particles according to the present invention as described above and

at least one additional detectable security feature, in particular an optically, machine or haptically detectable security feature.

Optically detectable security features are those which can be detected by without using an apparatus or with the help of a simple apparatus.

Machine detectable security features are those which can be detected by using an apparatus able to detect luminous, magnetic, electrically conductive, thermoelectronical or piezoelectronical properties.

Haptically detectable security features are those which can be detected by the human sense of touch.

In WO2006/045567 there can be found compounds which are added to obtain these additional detectable security features.

The core-shell particles according to the present invention and/or the colouring compositions can also be used for home care applications. The core-shell particles and/or compositions are used usually to give the product a specific visual appearance.

The colourant compositions of the present invention may be applied to any suitable substrate to colour at least a region of the substrate. A structural colour effect is produced due to direct reflection and/or diffraction of light in the wavelength of visible light by the core-shell particles. Substantially all of the light that is diffused by the core-shell particles is absorbed by the broad spectrum absorber contrast agent. This causes an enhancement of the structural colour effect. The substrate to be coloured can have any possible form as well as size.

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Materials for printing an coating include fibre (such as hair), skin, nails, food material, stone, ceramic, glass, paper, fabrics, wood, leather, metal (for example aluminium) and plastics.

The object to be coated can also be a combination of various substrates and it can have any form.

The coating and/or printing formulations according to the present invention are very suitable to colour (completely or in parts) packaging, which are for example used to sell commercial products, such as toothpaste containers, cans for drinks, shampoo containers, shower gel containers etc.

The colourant compound can also be used to print labels, which are then put onto a specific embodiment.

According to another aspect of the present invention, there is provided the use of a colourant composition as hereinbefore defined for colouring a substrate.

According to another aspect of the present invention, there is provided a method of colouring a substrate, which method comprises the step of contacting at least a region of the substrate with a colourant composition as hereinbefore defined.

It is not essential for the whole of the substrate to be contacted with the colourant composition. In other words, the coverage need not be complete, i.e. it can be discontinuous.

Suitable substrates include any substrate upon which a colloidal crystalline layer may form. Suitable substrates include, for example, fibre (such as hair), skin, nails, food material, stone, ceramic, glass, paper, fabrics, wood, leather, metal (for example aluminium) and plastics.

When the substrate is a food material, the colourant composition must be of a grade that can be used in food materials. Food materials in which the colourant compositions of the present invention may be used include, for example, eggs, fruit, vegetables, ice creams, sauces, water ice and chocolate.

For examples when vegetables or fruits are used, it is possible to coat the parts and/or print onto the parts which can be eaten as well as the parts, which are (usually) not eaten, like the peel, leaves, etc.

When the substrate is a plastics material, the colourant composition of the present invention may be dispersed in the plastics material, which may then be moulded for example by injection moulding, injection blow moulding or blow moulding.

The substrate may further comprise a protective material, for example as a protective covering or coating. The protective covering or coating may, for example, comprise a clear lacquer layer on a surface of the colloidal crystalline layer. Alternatively, the protective material may be formed *in situ*, for example by providing monodisperse particles having appropriately modified surfaces.

Thus, according to one aspect of the present invention, there is provided the use of a colourant composition as hereinbefore defined for colouring the hair of an individual.

There is also provided a method of colouring the hair of an individual which method comprises the step of contacting at least a region of the hair of the individual with a colourant composition as hereinbefore defined such that a colloidal crystalline layer forms on the hair.

There is also provided a hair dye composition comprising a colourant composition as hereinbefore defined.

The hair dye compositions of the present invention may be in any suitable form. For example, the hair dye compositions may be in the form of sprays, lotions, shampoos, creams or pastes which can be applied directly to all or part of the hair. Following a suitable contact time, excess composition can then be washed off if necessary.

According to another aspect of the present invention, there is provided the use of a colourant composition as hereinbefore defined for colouring a fabric.

Colouring of fabrics includes the ‘brightening’ of fabrics, such in the case of white textile materials.

According to another aspect of the present invention, there is provided a method of colouring a fabric which method comprises the step of contacting at least a region of the fabric with a colourant composition as hereinbefore defined.

Colorant compositions for use in colouring fabrics can be applied as part of standard laundry formulations known in the art such as powders or tablets that dissolve/disperse in water or as liquids.

According to another aspect of the present invention, there is provided a fabric dye composition comprising a colourant composition as hereinbefore defined.

Suitable fabrics include natural and synthetic fabrics. Examples of natural fabrics include wool, silk, fur, cellulosic materials such as cotton, flax, linen and hemp. Synthetic fabrics include, for example, viscose, nylon (polyamide), acrylic (polyacrylonitrile), aramid (aromatic polyamide) and polyester. The fabric may be in any suitable form, for example woven, non-woven or knitted.

The fabric dye composition of the present invention may be in any suitable form. For example, the fabric dye composition may be in the form of a solid, a liquid or a paste.

According to another aspect of the present invention, there is provided the use of a colourant composition as hereinbefore defined for colouring paper.

According to another aspect of the present invention, there is provided a method of colouring paper which method comprises the step of contacting at least a region of the paper with a colourant composition as hereinbefore defined.

By the term “paper” we mean any material that is manufactured in sheets from the pulp of wood or other fibrous substances and that is manufactured for any use, including for example writing or printing on, wrapping or packaging.

According to another aspect of the present invention, there is provided an ink composition comprising a colourant composition as hereinbefore defined. For example, the ink composition is suitable for printing on a printable surface such as paper or fabric.

Ink compositions of the present invention can typically be applied to a substrate using standard printing techniques known in the art for applying inks to a range of substrates. Typically, the ink compositions are applied to the substrate to form letters, numerals and/or other symbols, and/or graphic designs.

When the colourant compositions of the present invention are used to colour natural substrates, such as hair, nail, tooth and natural fabrics such as wool or cotton, the compositions typically comprise from 0.01 to 4% (preferably from 0.01 to 4%) by weight of the inverse colloidal crystals. When the colourant compositions of the present invention are used to colour synthetic substrates, the compositions typically comprise from 0.5 to 30% (preferably from 1 to 20%) by weight of the inverse colloidal crystals.

The various features and embodiments of the present invention, referred to in individual sections above apply, as appropriate, to other sections, *mutatis mutandis*. Consequently features specified in one section may be combined with features specified in other sections, as appropriate.

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and products of the invention will be apparent to those skilled in the art without departing from the scope of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are apparent to those skilled in the relevant fields are intended to be within the scope of the following claims.

Description of the figures:

Fig. 1: Synthesis of Core-shell particles with a PS core, a PMMA interlayer and a PEA shell.

The present invention will now be described further with reference to the following non-limiting examples.

Example 1

Core-shell particles of polymeric styrene-methyl methacrylate-ethyl acrylate (PS-PMMA-PEA) with Alizarin blue black are made by stepwise emulsion polymerization (Fig. 1).
A 500 ml four-necked flask fitted with a reflux condenser and a mechanical stirrer is charged with 100 ml reagent Milli-Q water, 6.9ml styrene, 2.5 mg alizarin blue black, 0.69 ml butylenedioldiacrylate as cross-linker and 0.1g Sodium dodecyl sulphate (SDS) as surfactant. The flask is put in an oil bath at 343K and flushed with nitrogen. The solution is stirred for 30min. Then 0.1 g ammonium peroxodisulfate and 0.1 g sodium hydrogen sulfite as a redox initiator system are added fast at once. During polymerization, the solution is stirred. After 3 h reaction time, a rigid core of polystyrene (PS) is formed. And then 13.g of methyl methacrylate (MMA), 7.5g Allyl methacrylate (ALMA), 0.01g ammonium peroxodisulfate, 0.01 g sodium hydrogen sulfite and 0.01 g SDS are added dropwise to the solution in 1 h in order to ensure that the reaction is under starved-feed

condition. After 2 h reaction time, the rigid core of polystyrene is coated with a layer of PMMA. And then 18g of ethyl acrylate (EA), 0.02g ammonium peroxodisulfate, 0.02 g sodium hydrogen sulfite and 0.01 g SDS are added dropwise to the solution in 2 h. After 3 h reaction time, the polymerization is ended and the product is isolated. All the processes are run continuously under starved-feed conditions.
The yield is between 70 - 85 wt-%.

Example 2

The core-shell particles of polymeric methyl methacrylate - ethyl acrylate (PMMA-PEA) with encapsulated black dye (Alizarin blue black) are made by stepwise soap-free emulsion polymerization in 2 steps. It starts with the polymerization of MMA using KPS as an initiator and ALMA as a cross-linker. In the second step, the PEA chains are grafted onto the PMMA core, specifically onto the allylic double bonds of ALMA. PEA must not be cross-linked.
The synthesis of the core shell spheres is carried out in a 500 ml four-necked flask fitted with a reflux condenser and a mechanical stirrer. The flask is charged with 10mg alizarin blue black and 140 ml reagent Milli-Q water. The flask is heated to 343K by an oil bath and additionally flushed with nitrogen. 6 ml MMA is added into flask and the mixture solution is stirred. The flask is continuously heated to 363K. After that, 0.5 g potassium peroxodisulfate in 10 ml water is added at once. After 2 h reaction time, a core of PMMA is formed. Then 4 ml EA is added dropwise within 2 h. After 3 h reaction time, the polymerization is finished and a core-shell particle is obtained in yield of 70 - 85% is obtained..

Example 3

Core-shell particles of polymeric benzyl methacrylate-ethyl acrylate (PBMA-PEA) with black dye (Alizarin blue black) are made by stepwise emulsion polymerization
The synthesis of the core shell spheres is carried out in a 500 ml four-necked flask fitted with a reflux condenser and a mechanical stirrer. The flask is charged with 10mg alizarin blue black and 140 ml reagent Milli-Q water. The flask is heated to 343K by an oil bath and additionally flushed with nitrogen. 6 ml BMA is added into flask and the mixture solution is stirred at 300 rpm. The flask is continuously heated to 363K. After that, 0.5 g potassium peroxodisulfate in 10 ml water is added at once. After 2 h reaction time, a core

of PBMA is formed. Then 4 ml EA are added dropwise within 2 h. After 3 h reaction time, the polymerization is finished and a core-shell particle is obtained in a yield of 70 - 85%.

Example 4

Core-shell particles of polymeric methyl methacrylate-ethyl acrylate (PMMA-PEA) with black pigment (Magnetite nanoparticles) are made by stepwise emulsion polymerization. First of all, aqueous dispersions of magnetite nanoparticles are prepared by a coprecipitation described in literature (S. Sacanna, A. P. Philipse. *Langmuir,* **2006**, *22(24),* 10209). Briefly, an aqueous solution of hydrochloric acid (10 mL, 2 M) containing FeCl2 (2 M) is mixed with 40 mL of $FeCl_3$ aqueous solution (1M) and afterward added to 500mLof ammonia (0.7 M). The obtained magnetite particles are easily sedimented by placing a magnet under the reaction vessel. The magnetite precipitate is then redispersed in 50 mL of tetramethylammonium hydroxide (1 M) and allowed to repeptize overnight to obtain an alkaline ferrofluid.

Secondly, these magnetite nanoparticles are treated with TPM(3-methacryloxypropyl trimethoxysilane. A dispersion of 2ml obtained alkaline ferrofluid was mixed with 0.1ml of TPM, 30ml alcohol and 70ml Milli-Q water under stirring. The treatment with TPM introduces double bonds on the surface of magnetite nanoparticles for the polymerization later.

Finally, PMMA-PEA core-shell colloids with encapsulated magnetite nanoparticles are prepared according to a standard emulsion polymerization. A 250 ml three-necked flask fitted with a reflux condenser and a mechanical stirrer is charged with 100 ml modified magnetite solution, 50 ml reagent Milli-Q water and 5mg SDBS as surfactant. The flask is put in an oil bath at 343K and flushed with nitrogen. The solution is stirred and 0.1 g potassim peroxodisulfate is added fast at once. After 30min, 4.5 ml MMA and 0.5ml allyl methacrylate are added to solution for polymerization. After 3 h reaction time, a magnetic core of PMMA is formed. And then 4 ml EA iss added dropwise to the solution in 1 h in order to ensure that the reaction iss under starved-feed condition. After 2 h reaction time, the magnetic core of PMMA iss coated with a soft layer of PEA.

CLAIMS

1. Core-shell particles, wherein there is a difference Δn of at least 0.001 (preferably 0.01, more preferably 0.1) between the refractive indices of the core material and of the shell material, characterised in that
at least one broad spectrum absorber contrast agent and/or at least one precursor material of a broad spectrum absorber contrast agent is encapsulated in the core-shell particle.

2. Core-shell particles according to claim 1 wherein the broad spectrum absorber contrast agent and/or the precursor material of a broad spectrum absorber contrast agent is encapsulated in the core part of the core-shell particle.

3. Core-shell particles according to claim 1 wherein the broad spectrum absorber contrast agent and/or the precursor material of a broad spectrum absorber contrast agent is encapsulated in the shell part of the core-shell particle.

4. Core-shell particles according to claim 1 wherein the broad spectrum absorber contrast agent and/or the precursor material of a broad spectrum absorber contrast agent is encapsulated in the core part and in the shell part of the core-shell particle.

5. Core-shell particles according to any of the preceding claims, wherein the broad spectrum absorber contrast agent is a mixture of compounds wherein that mixture has the same absorption property as a single broad spectrum absorber contrast agent.

6. Core-shell particles according to any of the preceding claims, wherein the broad spectrum absorber contrast agent is chosen from the group consisting of Ag, Alizarin Blue Black, Brilliant Blue Black, carbon black, iron hydroxide, iron oxide black and silver oxide black.

7. Core-shell particles according to any of the preceding claims, wherein the precursors of the broad spectrum absorber contrast agent is chosen from the group consisting of metal salts, preferably hydrophilic metal salts, such as nitrates or halogenides.

8. Core-shell particles according to any of the preceding claims, wherein the precursors of the broad spectrum absorber contrast agent is chosen from the group consisting of K, Ca, Sr, Ba, Zn, Pb, Fe, Ni, Ce, Co, Cr, Cu, Mn, Sn, Al, Ag, Mg, Au, Cd, Ag nitrate, Ag halogenide, Fe nitrate and Fe halogenide.

9. Core shell particles according to any of the preceding claims wherein the shell consists of a material which is filmable.

10. Core shell particles according to any of the preceding claims the core consists of a material, which is essentially form-stable.

11. Core-shell particles according to any of the preceding claims, wherein the core may be composed of an organic polymer, such as a polyurethane, polycarbonate, polystyrene, an acrylic polymer, an alkyd polymer, polyester, siloxane polymer, polysulfide, an epoxy-containing polymer or a polymer derived from an epoxy-containing polymer and, preferably, is cross-linked or of an inorganic polymer, such as a metal oxide (e.g. alumina, silica or titanium dioxide) or a semiconductor (e.g. cadmium selenide).

12. Core-shell particles according to any of the preceding claims, wherein the shell is formed from polyurethanes, acrylic polymers, alkyd polymers, polyesters, siloxane-containing polymers, polysulfides, epoxy-containing polymers, and polymers derived from epoxy-containing polymers.

13. Core-shell particles according to any of the preceding claim, wherein the weight ratio of core:shell is 1:100 to 100:1, preferably 1:10 to 50:1. more preferably 1:3 to 25:1.

14. Core-shell particles according to any of the preceding claims, comprising up to 3 wt-%, based on the total weight of the core-shell particles, of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent.

15. Core-shell particles according to any of the preceding claims, comprising 0.0001 to 1 wt-%, preferably 0.0001 to 0.5 wt-%, based on the total weight of the core-

shell particles, of at least one broad spectrum absorber contrast agent and/or at least one precursor of a broad spectrum absorber contrast agent.

16. Process for producing core-shell particles according to any of the preceding claims, which a two-step one-pot process.

17. Use of core-shell particles according to any of claims 1 – 15 in a colourant composition.

18. A colourant composition comprising core-shell particles according to any of claims 1 – 13.

19. A colourant composition according claim 18 comprising from 0.01 wt-% to 70 wt-%, based on the total weight of the colouring composition, of core-shell particles.

20. A colourant composition according to claim 18 and 19 comprising
(b) at least one solvent.

21. A colourant composition according to any of claims 18 – 20 comprising
(b1) water, and
(b2) optionally at least one solvent, chosen from the group consisting of alcohols, esters, ketones, ethers and aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

22. A colourant composition according to any of claims 18 – 21 comprising
(b) at least one solvent, chosen from the group consisting of alcohols, esters, ketones, ethers and aliphatic and aromatic hydrocarbons having at least six carbon atoms and mixtures thereof including refinery distillation products and by-products.

23. A colourant composition according to any of claims 18 – 22 comprising
(a) 0.01 wt-% to 70 wt-%, based on the total weight of the colourant composition, of the core-shell particles.

24. A colourant composition according to any of claims 18 – 21 comprising

(b) 30 wt-% and 99.99 wt-%, based on the total weight of the colourant composition, of at least one solvent.

25. A colourant composition according to any of claims 18 – 24 comprising
(c) at least one curing material, and
(d) at least one initiator.

26. A colourant composition according to claims 25, wherein the curing agent is chosen from the group consisting of epoxy acrylates, polyurethane acrylates, polyester acrylates, acrylated polyols and acrylated polyethers.

27. A colourant composition according to claims 25 and 26 comprising 0.01wt-% - 15wt-%, based on the total weight of the colourant composition, of the colourant composition.

28. A colourant composition according to any of claims 25 – 27, wherein the initiator is chosen from the group consisting of peroxide or peroxide containing compounds, benzophenone and benzophenone derivatives, acetophenone and acetophenone derivatives, benzoin ether derivatives, thioxanthones derivatives.

29. A colourant composition according to any of claims 25 – 28 comprising 0.01 wt-% - 15 wt-%, based on the total weight of the colourant composition, of at least one initiator.

30. A colourant composition according to any of claims 18 - 29 comprising
(e) at least one auxiliary.

31. A colourant composition according to claim 30 comprising
(e) at least one auxiliary chosen from the group consisting of wetting agents, buffer substances, antistatic agents, bleaching agents, oxidation agents, rheology modifiers, solubilizers, siccative, antifoams, levelling agents, surfactants, foam suppressants, antifreezing agents or fungistatic and/or bacteriostatic agents, optical brighteners, softeners, flameproofing additives, or dirt repellents, water repellents and oil repellents, as well as water softeners and natural or synthetic thickeners, e.g. alginates and cellulose ethers.

32. A colourant composition according to claim 30 and 31 comprising
    (e) 0.1 wt-% to 10 wt-%, based on the total weight of the colourant composition, of at least one auxiliary.

33. A colourant composition according to any of claims 18 – 32, characterized in that it is in the form of a solid, liquid, a gel, mousse, wax or a paste.

34. A colourant composition according to any of claims 18 - 33, which is a coating formulation and/or a printing formulation.

35. A printing formulation according to claim 34, which is a used for Ink jet (such as Bubble Jet, Compound jet, Dry Inkjet, Hotmelt Inkjet), relief printing, intaglio, letterpress, lithography, flexography, gravure, screen printing and pad printing.

36. A colourant formulation according to claim 34, which is used for air knife coating, immersion (dip) coating, Gap Coating, Curtain coating, rotary screen, Reverse Roll coating, Gravure coating, Metering rod (Meyer bar) coating, Slot Die (Extrusion) coating and Hot Melt coating.

37. Use of core-shell particles according to claims 1 – 15 and/or at least one colourant compositions according to claims 18 - 33 in personal care formulations and/or cosmetic formulations.

38. Personal care formulation and/or cosmetic formulation comprising core-shell particles according to claims 1 – 15 and/or at least one colourant compositions according to claims 18 - 33 in personal care formulations and/or cosmetic formulations.

39. A security printing and/or coating ink comprising at least one inverse colloidal crystal according to claim 1 - 15.

40. Use of a colourant composition according to claims 18 – 37 and 39 for colouring a substrate.

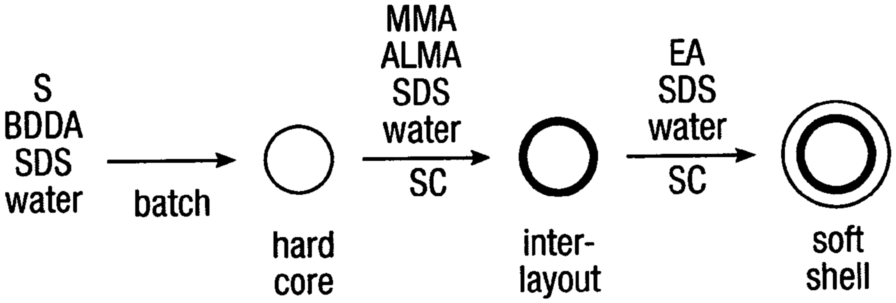
41. Use according to claim 40, wherein substrate is chosen from the group consisting of fibre (such as hair), skin, nails, food material, stone, ceramic, glass, paper, fabrics, wood, leather, metal (for example aluminium) and plastics.

42. Substrate printed and/or coated with a colourant composition according to claims 18 – 36 and 39.

43. Substrate according to claim 42, which is chosen from the group consisting of fibre (such as hair), skin, nails, food material, stone, ceramic, glass, paper, fabrics, wood, leather, metal (for example aluminium) and plastics.

Fig.1.

Synthesis of Core-Shell particles with a PS core, a PMMA interlayer and a PEA shell.



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/055822

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K9/10 C08F292/00 C08F2/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 082 757 A (KEOSHKERIAN BARKEV [CA] ET AL) 21 January 1992 (1992-01-21) claims 1,9-14,18; example 1	1-43
X	US 4 954 412 A (BRETON MARCEL P [CA] ET AL) 4 September 1990 (1990-09-04) column 11, lines 5-41; claims 1,7,26,28-30; example 1	1-43
X	US 5 990 202 A (NGUYEN KHE C [US] ET AL) 23 November 1999 (1999-11-23) claims 1-5,22-24,28-33; figure 1a	1-43
X	EP 1 445 288 A (ROHM & HAAS [US]) 11 August 2004 (2004-08-11) paragraphs [0022], [0085] - [0088]; claims 1,3,4,6; example 1	1,2,6, 9-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 25 September 2008	Date of mailing of the international search report 07/10/2008
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Sperry, Pascal

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2008/055822

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 5082757	A	21-01-1992	NONE			
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