

Inorganic Particles Treated With Phosphonated Siloxane

The invention is concerned with inorganic particles coated with at least one reactive organic silane compound, a process for the preparation of inorganic particles treated with a organophosphonatosiloxane and their application.

In order to allow inorganic particles to be uniformly dispersed and built into a (plastic) matrix, it can be necessary to modify the surface of the particle. An inorganic particle, as for example, a titanium dioxide pigment, has by nature hydrophilic properties and it should, in order to be dispersed optimally, for example in polyethylene, exhibit a hydrophobic character. Such a modification of the particle is usually achieved via a coating with an organic substituent ("organic treatment"). In order to achieve a coating stable against stripping, the organic substance must be chemically bound to the particle, something that requires special measures.

In a publication of Huels AG "Applications of Organofunctional Silanes - DYNASILANE" (1989) page 10 following, the treatment of particles with organofunctional silanes is described: Originating with a silane substituted with at least one organic residue and with silicon functional residues, silicon via a hydrolysis is fixed (chemically bound) via oxygen to the pigment surface, whereby an oligomerization also takes place, i.e. a build up of a polysiloxane lattice and with that an effective covering of the pigment surface. The organic substituent directly on the silicon atom, e.g. an octyl residue, provides that the pigment particle will show hydrophobic properties and a good dispersibility.

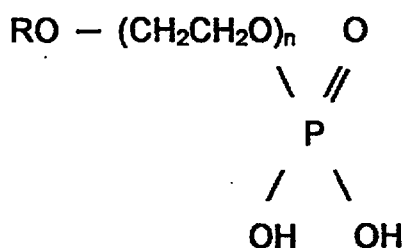
Also a post-treatment of inorganic particles with organic phosphorus compounds as a rule improves the dispersibility and alters the hydrophilic behavior.

In the DE AS 12 34 234 it is recommended that in the improvement of the dispersibility the particles be coated with an acidic organic phosphorus compound, as for example, a mono- or diorthophosphoric ester. Indeed, although in this manner organic residues are

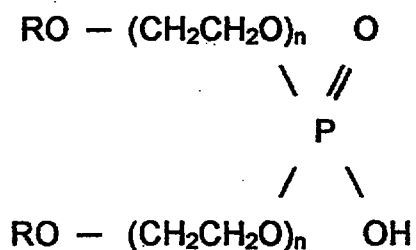
allowed to bond to a particle surface, a lattice coating cannot be achieved with such phosphorus organic groups.

In the DE 30 15 766 A pigments are coated with phosphorus polysiloxanes; the phosphorus groups carry no organic substituents the process is expensive and no control of the hydrophobicity is possible.

In the DE 15 92 905 or the EP 0 496 150 titanium dioxide pigments are treated with ester of phosphoric acid of the following general formulae for improvement of dispersibility in an organic or aqueous medium.



or



In the US 4 183 879, US 4 209 430 and EP 0 707 051 phosphonates (salts and esters or phosphonic acids) are described, which are brought as coatings onto pigments whose properties are improved, especially the "yellowing" is said to be avoided.

In the EP 0 073 343 titanium dioxide pigments are modified with an organophosphate/alkanolamine addition product and a polyol.

An interlaced structure stably bound chemically to the surface of the inorganic particle is not achieved with all these materials.

In the WO 97/20001 it is generally elucidated on the top of page 2 that unreactive organic phosphorus compounds are bound electrostatically to the pigment surface and in the processing of such pigment, these organic residues desorb from the pigment and represent an undesirable additive in the matrix. Especially in the plastics processing industry, desorption effects lead to disturbances in the surface of the plastic production part and quite severely impair the printability and heat sealability.

In all attempts up to now to better anchor organic phosphorus compounds with reactive groups to the particle surface, no interlaced coating was obtained. With phosphonates of the type $R_1P(O)OR_2OR_3$ a reaction with the pigment surface is possible, however at most two groups can form a chemical bond with each other so that a net-like development of an organophosphonate structure as in the case of a polysiloxane is in this way also not possible.

The invention concerns inorganic particles with an interlaced organic covering via an organopolysiloxane, in which organic phosphonate compounds are built in and in which at the very least, the silicon atoms are bonded chemically (via oxygen) largely to the particle surface.

The object of the invention is also a process for the preparation of inorganic particles, which are coated with interlaced organophosphonatosiloxanes.

Also the object of the invention is the use of organophosphonatosiloxane-treated pigments in plastics and paint systems, as well as in paper and fiber pigmenting.

In the case of inorganic particles of this invention, the organophosphonate compound is not added on absorptively to the surface, but chemically bonded. Without defining the

exact scientific interpretation, the useful concept has evolved that in the interlaced polysiloxane bonded with the surface, organophosphonate groups are chemically tied in, and although, as a rule, no chemical bond is provided directly from the phosphorus atom to the particle surface, the phosphonate groups, because of their bonding to one or two of the silicon groups bonded to the particle, cannot be chemically removed easily.

Through the "mixing" of the phosphorus and silicon groups in a network about the inorganic particle a certain "elasticity" of the coating is achieved. It may also be that one of the reactive groups of the organophosphonate compound is bonded directly to the particle surface and only the second function is bonded with an organosilicon group or also the two organophosphonate compounds are bonded directly amongst themselves and with the particle surface and can be present almost as an island in a polysiloxane network.

The special advantage of such organically coated inorganic particles of the invention can be seen in the fact that the phosphorus-carbon bond is very stable, and therefore the organic substituents situated on phosphorus are no longer separated in the subsequent treatment of the particle, especially in the insertion into organic matrices, and at the same time the variety of possible organic chains permits an optimization of the product properties, for example the hydrophobic/hydrophilic behavior.

As inorganic particles with an organic coating of the invention, pigments and extenders are especially suitable. Quite especially preferred is the organic treatment in the case of titanium dioxide pigments, which are produced according to the sulfate or chloride process, and can exhibit the anatase or rutile structure.

In the preferred method the inorganic particles, before they are treated organically, are post-treated inorganically, i.e. they first receive on the particle surface a coating of metal oxides, hydroxides or phosphates. Especially preferred in the case of titanium dioxide pigments is a surface treatment with aluminum oxide.

The inorganic particle coated with interlaced phosphonosiloxane (at least partially) can exhibit not only uniform but also differing organic residues on the phosphorus and/or silicon atom. On the silicon atom alkyl, alkenyl, cycloalkyl and aryl residues are possible, on which for their part they can be substituted with oxygen or nitrogen functional residues such as amine, epoxy or methacryl residues. In like manner the organophosphonate compounds of the invention bonded with the polysiloxane and/or directly bonded to the particle surface can exhibit uniform or different organofunctional residues. For the organic residue on the phosphorus atom, besides the same residues as with silanes, imine, carboxyl or hydroxyl residues also come into consideration. The number of carbon atoms amounts preferable to 1 to 16, with cycloalkyl groups at least 5, with pure aryl groups at least 6.

In the process of the invention for the preparation of inorganic particles with silicon and phosphorus organic compounds chemically bound to the particle surface, in which these compounds are predominantly interlaced with one another, one starts with organosilicon and organophosphonate compounds, which respectively show reactive residues, in which the hydrolytic splitting of this residue results in the chemical fixation of the compound on the particle surface or on a bound neighboring group.

Alkoxy, hydroxy, but also halogen are well known and suitable as reactive residues for the organosilane compound. The reactive residues in the organophosphonate compounds are in essence the same as with silanes. In addition, the phosphonate compounds can be present as alkali or ammonium salts.

Of special advantage is the possibility of widely altering and optimizing the organic coating about the inorganic particle via the invention. It is not at all dependent on a stoichiometric ratio of silicon and phosphorus organic compounds. On the contrary products can be used with a differing ratio of constituents, mol ratios of 10:1 to 1:10 are preferred and with a differing quantity, weight portions of 0.05 to 5% based on the

inorganic particle are preferred. Corresponding fine tunings are conducted by the specialist if he exactly knows the end application.

The hydrophilic/hydrophobic character of an inorganic particle is adjustable via the type and the portion of the organophosphonate compound. Processing properties, such as dispersibility, inclination to dust, wettability, processibility and lacing are altered by the replacement of silicon organic groups by phosphorus organic groups. A better stability ("PVC greying") is achieved. There also can be economic advantages.

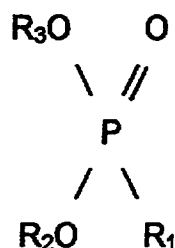
The overall treatment of the base material must not be altered by the process of the invention; for example, with titanium dioxide in the scope of an inorganic surface treatment, a layer of inorganic oxides, such as for example Al_2O_3 , MgO , SiO_2 , ZrO_2 , preferably Al_2O_3 , can first of all be brought in the aqueous phase. For that purpose a media milled (if necessary) titanium dioxide suspension, which can contain polyphosphates, aminoalcohols or acrylates, for example, as dispersing agents, is treated with salts of the inorganic oxides, preferably with aluminum salts and by altering the pH, the corresponding oxide hydrate precipitates.

The organophosphonate and organosilicon compounds are incorporated in the following manner: the pH of a titanium dioxide suspension is adjusted to values between 2 and 11, preferably between 3 and 5 by addition of common acids and bases, such as HCl , H_2SO_4 , NaOH , KOH . It is also possible, however, in the case of a preceding inorganic surface treatment, to steer toward the desired pH through the selection of the treatment chemicals and the carrying out of the treatment. The temperature lies between 20 and 80 °C, when the organics are added into the aqueous suspension.

If the organosilicon and organophosphonate compounds, themselves hydrolysis prone liberate substances, as for example hydrochloric acid in the case of chlorosilanes, which lead to a pH alteration, a further pH correction through addition of the above named chemicals can be necessary, the phosphorus and organosilicon compounds are not pre-mixed with one another, but are added separately simultaneously or sequentially to the

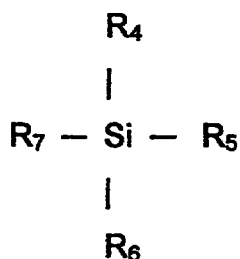
titanium dioxide suspension. As is generally common in the post-treatment of pigments certain holding times combined with stirring are to be observed.

As organophosphonate compounds phosphonates of the general formula



come into consideration, in which R_1 is a non-hydrolyzable alkyl, cycloalkyl or aryl residue with 1 to 16 carbon atoms, in which R_1 exhibits in the case of pure cycloalkyl residues at least 5 carbon atoms, in the case of pure aryl residues at least 6 carbon atoms and R_1 in addition to the above cited alkyl, cycloalkyl and aryl residues can still carry one or more substituents, which are nitrogen and/or oxygen functional, such as amine, imine, carboxyl, hydroxyl residues or the like (also mixtures with different R_1 residues are possible) and R_2 or R_3 can be either both or individually an alkyl residue or hydrogen or a univalent metal cation, such as Na^+ , K^+ , or NH_4^+ (also mixtures are possible).

As organosilicon compounds silanes of the following general formula are used



in which R_4 is a non-hydrolyzable alkyl, alkylene, cycloalkyl or aryl residue with 1 to 20 carbon atoms and R_4 exhibits in the case of alkyl residues at least 2 carbon atoms, in

the case of cycloalkyl residues at least 5 carbon atoms, in the case of pure aryl residues at least 6 carbon atoms and R_4 in addition to the above cited alkyl, alkylene, cycloalkyl or aryl residue can still bear one or more substituents, such as amino, epoxy, methacryl residues, R_5 , R_6 , and R_7 can be the same or different hydrolyzable residues from alkoxy, acetoxy, hydroxy, halogen or mixtures therefrom.

The organosilicon compound can be also consist of silane hydrolysates, such as are described in the European Patent Application 0 518 057.

After the inorganic and organic treatment the inorganic particles are separated and dried with common procedures.

It is also possible to suitably dry a titanium dioxide suspension directly, for example a spray drying, without filtering and washing.

As a rule, after drying a grinding follows, as for example a steam jet grinding. In this grinding, if need be, the addition of additional organic substances such as polyalcohols, silicon organic substances, for example silicon oils or silane hydrolysates can ensue.

The inorganic particles of the invention, preferably titanium dioxide pigments, can find application in plastics and paint systems, for example in polyethylene, polypropylene, polybutylene and copolymers of polyethylene, vinyl acetate, polyvinyl chloride, polyvinyl ester, polystyrene, polyamide, polyester, polyurethane, polycarbonate, polyimide, alkyd, epoxide.

Especially preferred is a use in polyethylene, polypropylene, polystyrene and polyvinyl chloride, especially in the production of PE-masterbatches for paper coating and the extrusion of films.

Additional areas of use lie in the realm of paper and fiber pigmenting.

The invention is further elucidated with the aid of examples as follows.

The judgement of the products follows according to dispersibility, ability to be stripped off and water wettability, which are briefly described first of all in the following.

Dispersibility Test

In the dispersibility test in polyethylene (PE) a 50 % concentrate (masterbatch, MB) is prepared in PE-LD. For the determination of the dispersibility, the pressure rise is determined, which occurs in the extrusion through a 25 mm sieve with a Brabender measuring extruder under special test conditions.

At the beginning of each test 400g PE-LD, MFI (190 °/2,16 kg) = 20 g/10 min, are extruded through the screen at a screw rotational speed of 120 min⁻¹, until a constant pressure P_1 occurs. Without interruption of the extrusion 1 kg of the respective 50 % titanium dioxide concentrate is subsequently extruded through the screening stack at the same screw rotational speed.

When the total quantity of concentrate is extruded through the screen, the extruder is momentarily run empty so that the pressure suddenly falls and with that a characteristic final pressure P_2 can be read.

As a measure of the pressure increase from 1 kg MB (50 % titanium dioxide)

$$\Delta P = P_2 - P_1$$

applies.

After each test extruder and screening stack are flushed again with unpigmented PE-LD and cleaned. After disassembly of the screen a new screening stack is used for the next test, and as briefly described, reprocessed.

Outstandingly suitable titanium dioxide pigments exhibit ΔP values < 50 bar/kg.

Test for Ability to be Stripped

10 grams of the pigment to be investigated are mixed with 50 ml methanol and digested at $60\text{ }^{\circ}\text{C}$ for 4 hours. Subsequently one allows cooling to room temperature and centrifuges. The organic phase is weighed after evaporation and in the case of a measurable residue is tested with the aid of analytical methods (for example FT-IR). The separated pigment is dried at $110\text{ }^{\circ}\text{C}$, homogenized and the carbon and phosphate content determined by the usual methods.

The difference of the carbon- or phosphorus-content before and after the extraction serves for judgement of the splitting off behavior. At differences in before and after carbon-content $< 10\%$ or differences in before and after phosphorus-content $< 10\%$, an organic compound is considered non-removable. For another, the quantity of residue and its analytical correlation to the organic compound employed are recruited for judgement of the splitting off behavior.

Carbon or Phosphorus Retention

Under carbon or phosphorus retention the recovery proportion of the organic compound is to be understood, which was used for treatment, expressed as carbon or phosphorus content.

Water Wettability

A small quantity of pigment is applied to the surface of distilled salt water (room temperature). Hydrophobic products even after stirring are not wetted and remain on the surface of the water. Hydrophilic products immediately sink below the surface. Partially hydrophobic products are wetted after dropwise addition of methanol.

The appraisal is listed: hydrophobic - partially hydrophobic - partially hydrophilic - hydrophilic.

In all the following examples, a titanium dioxide base material prepared according to the chloride process is used. An alkaline suspension is prepared in the well known way with use of hexametaphosphate as dispersing agent and is ground in a sand mill. The pigments in suspension are in the well known way provided with Al_2O_3 layer (0.2 % based on titanium dioxide).

Example 1 (Comparison Example)

A sand milled titanium dioxide suspension is treated with stirring at $\text{pH } 7.25 \pm 0.25$ with 0.2 % of an alkali phosphonate with the trade name LOPON WN of BK Giulini Chemie and filtered after a retention time of 60 minutes, washed with water and dried. A steam-jet grinding common in the titanium dioxide industry follows. The pigment so obtained is subjected to the tests cited above. For the result see Table 1.

Example 2 (Comparison Example)

A sand milled titanium dioxide suspension is treated under stirring at $\text{pH } 7.5 \pm 0.25$ with 0.4 % octyltrichlorosilane and for maintenance of the pH at the level cited above, 10 % NaOH is added. After a retention time of 60 minutes, the titanium dioxide is filtered off, washed and dried. A steam-jet grinding common in the titanium dioxide industry follows. The pigment thus obtained is submitted to the test cited above. See Table 1 for the results.

Example 3

To a sand milled titanium dioxide suspension are added with stirring at $\text{pH } 7.25 \pm 0.25$ simultaneously, but separately 0.4 % octyltrichlorosilane and 0.2 % alkali phosphonate LOPON WN. An addition of 10 % NaOH follows to maintain the pH in the above cited range. After a retention time of 60 minutes, the titanium dioxide is filtered off, washed, dried and followed by a steam-jet grinding. The pigment thus obtained is subjected to the tests cited above. For results see Table 1.

Example 4

Conducted as example 3, however with the difference that 0.5% octyltrichlorosilane and 0.1 % alkali phosphonate LOPON WN are used.

As can be gathered from examples 3 and 4 in comparison to examples 1 and 2, a very good dispersibility can be achieved via the mixed organic interlaced coating of the pigments. At the same time the water wettability is adjustable to requirements. The retention in both cases lies above 90 %, something which is contingent upon the chemical bond of the organic phosphorus group either directly or on silicon on the pigment.

Example 5

To a sand milled titanium dioxide suspension under stirring a sodium aluminate solution is added, whose quantity is equivalent to 0.2 % Al_2O_3 . The pH should not exceed 8 to 9 in the addition. After the addition and 10 minutes retention time an adjustment of the pH to 7.25 ± 0.25 with 10 % HCl follows. At this pH 0.5 % octyltrichlorosilane and 0.2 % LOPON WN are added simultaneously and with stirring. Addition of 10 % NaOH follows for maintenance of the pH in the above cited range. After a retention time of 60 minutes the titanium dioxide is filtered off, washed, dried, and followed by a steam-jet grinding. The pigment thus obtained is subjected to the tests cited above. For the results, see Table 2.

Example 6

Analogously to example 5 an inorganic treatment takes place with 0.2 % Al_2O_3 . After a 10 minute retention time octyltrichlorosilane is first of all added until the pH has fallen into the range 4.25 ± 0.25 . After that during the addition of the remaining octyltrichlorosilane this pH range is held constant through addition of 10 % NaOH. The entire amount of octyltrichlorosilane amounts to 0.5%. Then in the cited pH range 0.1 % alkali phosphonate LOPON WM is added. After a retention time of 60 minutes further processing is as described in Example 5. For the result see Table 2. The organic

treatment at a pH in the range of 3 to 5 shows to advantage in the retention of the compounds.

Example 7

Analogously to Example 5, a treatment with 0.2 % Al_2O_3 ensues. After the 10 minute retention time the pH is at 7.25 ± 0.25 through addition of 10 % HCl. Subsequently the simultaneous, not premixed addition of 0.5 % octyltriethoxysilane and 0.2 % 1-hydroxyethane-1,1-diphosphonic acid follows. The pH is adjusted during the addition in the above cited range via 10 % NaOH. After the retention time of 60 minutes, the titanium dioxide is filtered off, washed, dried and ground on a laboratory mill. For C/P retention, water wettability and strippability see Table 2.

Example 8

Processing is as in Example 7. At pH 7.5 ± 0.25 the simultaneous addition of 0.5 % octyltriethoxysilans and 0.2 % sodium N-octylamino-N,N-bis (methylenephosphonate) ensues. The pH is adjusted in the above cited range through the addition of 10 % HCl. Further processing is as described in Example 7.

Examples 7 and 8 show that the hydrophilic/hydrophobic properties can be influenced by the selection of specific functional phosphonates. Adversely, the low retention of the organics is portrayed.

TABLE 1

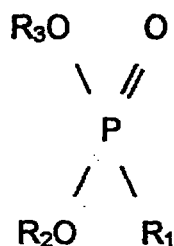
Example	Organic Treatment-Substance(s)	C/P Retention	Dispersibility Test (bar/kg. TiO₂)	Water Wettability	Ability to be Stripped Off
1	Alkali Phosphonate 0.2%	80%	640	Hydrophilic	<10%
2	Octyltrichloro-silane 0.4%	>90%	42	Hydrophobic	<10%
3	Alkali Phosphonate and Octyltrichloro-silane 0.2%/0.4%	>90%	23	Partially Hydrophilic	<10%
4	Alkali Phosphonate and Octyltrichloro-silane 0.1%/0.5%	>90%	35	Partially Hydrophobic	<10%

TABLE 2

Example	Inorganic Treatment Substance	Organic Treatment-Substance(s)	C/P Retention	Dispersibility Test (bar/kg TiO₂)	Water Wettability	Ability to be Stripped Off
5	0.2% Al ₂ O ₃	Alkali Phosphonate and Octyltrichloro-silane 0.2%/0.5%	>90%	49	Partially Hydrophobic	<10%
6	0.2% Al ₂ O ₃	Alkali Phosphonate and Octyltrichloro-silane 0.1%/0.5%	>90%	25	Partially Hydrophobic	<10%
7	0.2% Al ₂ O ₃	1-Hydroxyethane-1,1-Diphosphonic Acid and Octyltriethoxy-silane 0.2%/0.5%	>80%	Not tested	Hydrophilic	<10%
8	0.2% Al ₂ O ₃	Alkali Phosphonate and Octyltrichloro-silane 0.1%/0.5%	>65%	Not tested	Hydrophobic	<10%

Patent Claims

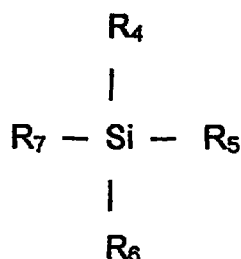
1. Inorganic particles, coated with at least one reactive organosilane compound, in which on account of their reactivity, the organosilane compounds have entered into chemical bonds with one another and with the particle surface and an organic polysiloxane has bonded to the particle, characterized by the fact that a part of the reactive organosilane compounds is replaced by reactive organophosphonate compounds.
2. Inorganic particles according to claim 1, characterized by the fact that between the particle and the organic coating at least one additional layer is present from among a metal oxide or phosphate or oxide hydrate.
3. Inorganic particles according to claim 1 or 2, characterized by the fact that the reactive organophosphonate compound is a phosphonate of the general formula



in which R_1 is a non-hydrolyzable alkyl, cycloalkyl or aryl residue with 1 to 16 carbon atoms, in which R_1 exhibits in the case of pure cycloalkyl residues at least 5 and in the case of pure aryl residues at least 6 carbon atoms (also mixtures with different R_1 are possible) and R_2 and R_3 can be either both or individually an alkyl residue, hydrogen, a univalent metal cation or ammonium (also mixtures are possible).



4. Inorganic particles according to claim 3, characterized by the fact that in the residue R_1 one or several hydrogen atoms is substituted by nitrogen and/or oxygen functional residues as amine, imine or hydroxyl.
5. Inorganic particles according to one or several of the claims 1 to 4, characterized by the fact that the reactive organosilane compound is a silane of the general formula,



in which R_4 is a non-hydrolyzable alkyl, alkylene, cycloalkyl or aryl residue with 1 to 20 carbon atoms, and R_4 exhibits in the case of alkylene residues at least 2 carbon atoms, with pure aryl residues at least 6 carbon atoms (also mixtures with different R_4 are possible) and in the case of R_4 moreover 1 or 2 hydrogen atoms can be substituted by nitrogen and/or oxygen functional residues as amino, epoxy or methacryl, and R_5 , R_6 and R_7 can be the same or different residues from among alkoxy, acetoxy, halogen or mixtures thereof.

6. Inorganic particles according to one or several of the claims 1 to 5, characterized by the fact that the particles are coated with uniform organosilane and uniform organophosphonate compounds.
7. Inorganic particles according to one or several of the claims 1 to 5, characterized by the fact that the particles are coated with mixtures of various organosilane and/or organophosphonate compounds.



8. Inorganic particles according to one or several of the claims 1 to 7, characterized by the fact that the mol ratio of the organosilane compounds to the organophosphonate compounds varies between 10:1 and 1:10.
9. Inorganic particles according to one or several of the claims 1 to 8, characterized by the fact that the coating quantity of the inorganic particle with organosilane compounds and organophosphonate compounds amounts to 0.05 to 5 % (based on the weight of the inorganic particle).
10. Process for the preparation of inorganic particles, which are coated with organosilane and organophosphonate compounds, which are chemically bonded with the particle surface and/or with one another, characterized by the following steps:
 - a) Dispersing the inorganic particle in an aqueous solution;
 - b) Adjusting the pH in the range 2 to 11, preferably 3 to 5;
 - c) Separate addition of the reactive organosilane and reactive organophosphonate compounds;
 - d) Post-adjusting the pH;
 - e) Stirring the suspension;
 - f) Filtering, washing, drying and grinding the inorganic particle.
11. Process according to claim 10, characterized by the fact that it proceeded from titanium dioxide, which had been prepared according to the sulfate or chloride process and exhibited an anatase or rutile structure.
12. Process according to claim 10 or 11, characterized by the fact that the inorganic particle was submitted to a wet grinding, for example a sand grinding.
13. Process according to claim 10, 11 or 12, characterized by the fact that the inorganic particles before the coating with reactive organosilane and reactive organophosphonate compounds are treated with oxides or phosphates, especially



preferred with Al_2O_3 of the quantity 0.1 to 0.5 weight % based on the inorganic particle.

14. Process according the claim 10, 11, 12 or 13, characterized by the fact that the inorganic particles are steam-milled after the drying.
15. Use of the inorganic particles according to one or several of the claims 1 to 9 in plastics systems or paint systems.
16. Use of the inorganic particles according to one or several of the claims 1 to 9 in the area of paper or fiber pigmenting.

