Along with the surface effects, nanoparticles in particular offer the possibility of integrating additional effects into the coating systems. In the next chapter, we will address the manufacture, manipulation, and application of selected nanoparticles.

### 3.5 Production and modification of nanoparticles

The production and modification of nanoparticles forms one of the most significant reaction principles in silane technology as shown in the diagram in Figure 3-2. One refers to the process of surface modification with silanes as silanization. In the following, a definition will be given of nanoparticles, a summary of the most significant production methods of nanoparticles, stabilizing, and the possibility of manipulation.

A commonly accepted definition of the term “nanoparticles” refers to a particle size under 100 nm. The bottom limit lies within the range of 1 nm. Any further reduction in size brings us to the size of molecules and atoms. According to a more precise definition which distinguishes the aspect of transparency, nanoparticles are so small that they no longer disperse any light, if they are found dispersed in a matrix. With a rising refraction index, in order to be invisible to light, particles must continue to get smaller. For example, with TiO$_2$-particles (n$_D$ = 2.6) in a polymer matrix (n$_D$ = 1.5), full transparency can first be expected starting with particle diameters under 30 nm. In reality, the last dispersing fogs do not disappear in dispersions until the particles are smaller than 15 nm. This definition is useful for someone who develops transparent scratch-resistant coatings, but not for someone who is integrating photo-catalytically active nanoparticles in a white wall-paint. A light clouding caused by the nanoparticles would not affect this procedure. Only the effects and a fine distribution have significance. Nanoparticulate powders are characterized by a particle surface in the range of 100 m$^2$/g. Particles with 4 to 5 nm particle size can achieve a surface of more than 500 m$^2$/g. One can picture that in this way:

If one lays 1 g of fine sand in the palm of their hand, then this has approx. the total surface of a small table (0.5 m$^2$/g). This just lies within the realm of the comprehensible. If one were to place 1 g of 5 nm SiO$_2$-nanoparticles in their palm, then one would be holding approx. the surface of a football field in their hand. This goes beyond the limits of our imagination. The appearance, the weight, and the composition are identical in this model. Only the particle size is

![Figure 3-40: Schematic presentation of the surface modification of metal oxides with silane](image-url)
different. In other words, these particles consist mostly of surface. Catalytic or optically effective filler coats are therefore always more active in nanoform, because the corresponding reaction takes place on the surfaces. Depending upon composition or crystallite-form of the nanoparticles, varying properties can be caused. For example, the nano-TiO₂ in its anatase-form is characterized by an increased photo-catalytic effect, and in its rutile-form, by increased UV protection, which can be used for sun-protection.

Nano powders and nano dispersions are especially inclined to aggregation. This effect is used in several materials. The dense agglomeration of nanoparticles during sintering gives modern ceramics and metals a high density and extreme solidity.

The particle aggregation is disruptive to dispersions and composites that should be transparent, or if an even distribution of the particles is advantageous to achieve the desired function. For this reason, one of the basic requirements for the processability of nanoparticles in modern lacquer systems is that a surface modification separates the particles from one another (see Chapter 3.5.2.1).

Soot and pyrogenic silicic acids (SiO₂) such as the “Aerosil” are among the classic nano powders. Others are various, often oxidic, pigments (TiO₂, Al₂O₃, ZrO₂). These inorganic materials are being developed intensively. Now there is a large selection of very diversified nano powders available. Especially in the Asian market, there is active growth in the number of suppliers, which is very good for the paint and lacquer industry. In Europe and especially in Germany, the focus of the research lies more in the fields of application for nano powder, so that the business exchange is flourishing in both directions.

In order to utilize nanoparticles, one should have knowledge of the basic principles of manufacture and characterization, in order to be in a position to evaluate one’s modifications appropriately.

### 3.5.1 Production of nanoparticles

When discussing the production of nanoparticles, the most common production will be discussed. The literature distinguishes the procedures by **bottom-up** or **top-down method**, according to production from the solid phase, the gas phase, or the liquid phase and/or by microbiological techniques. Since the top-down method usually involves complex equipment, the constructive synthesis (bottom-up) is far more common. Both methods can lead to nanometer sized dimensions in varying degrees. In the following, the most significant methods for the production of nanoparticles will be explained briefly.

#### 3.5.1.1 Top-down: ball grinding

One way to produce nanoparticles is done by solid phases. In this case, the microparticles are crushed into nanoparticles by shear force. Ball mills with grinding balls
made of hard ceramic or zirconium dioxide are especially effective for this method. The surfaces that are created during the crushing process are stabilized by surfactants. In this respect, one can refer to a modification of the nanoparticles. The ball mill is constructed out of a closed cylinder and a grinding agent (balls or short cylinders). The cylinder turns around the horizontal axle. The powder particles are crushed on both the grinding agent as well as the wall (Figure 3-41).

The efficiency of the grinding process is dependent on the relationship between the size, the specific weight and the solidity of the grinding substance and grinding agent. Heavy grinding agents are more efficient. One problem with ball grinding is the wear debris on the wall and on the grinding agents, which leads to contamination. The balls are made of hard materials, such as steel or tungsten carbide. These products are often not well suited for simple integration into lacquer systems, because mostly agglomerated products result. A common method of producing nanoparticles is the separation from the gas phase.

3.5.1.2 Bottom-up: production from the gas phase
The production of nanoparticles from the gas phase is considered a physical production method and also a bottom-up strategy. In this case, the solid reactants are transported into the gas phase by adding energy. Nanoparticles are created by condensation. No chemical reaction takes place with the source material, but instead merely a rearrangement occurs, as well as changes in the crystallite sizes and sometimes a phase transformation (see Figure 3-42).
The reactants, such as powder or electrodes from a mixture of reactants, are condensed under a protective gas by plasmas, arcs, heated filament or electron beams. This gas mixture, consisting of the protective gas and the reactant steam, is cooled quickly, so that the gas phase is supersaturated with the steam of the source material. It is now thermodynamically easier for the reactants to condense, or, nucleation and the production of nanoparticles occurs. For the reactant with the larger enthalpy of condensation (normally the metal), the nucleation is particularly advantageous, and therefore this forms the core of the coated nanoparticle. For the coating and stabilization, a second source material is often used, such as carbon, which accumulates as a coating on the core and encases it. Depending on the process and the nanoparticle core, this crystalline happens as graphite or in the form of amorphous carbon. With these methods, along with metal nanoparticles (Au, Pt,…) and alloys, also all possible rare earth particles can be produced (for example Gd$_2$C$_3$, Ho$_2$C$_3$ etc.). The “Aerosil” method is a special method for the production of nanoparticles.

### 3.5.1.3 Bottom-up: “Aerosil” method

A wide-spread method for the production of nanoparticles is the so-called “Aerosil” method\[63\]. “Aerosil” belongs to the family of the synthetic silicic acids and is produced by flame hydrolysis from siliciumtetrachloride according to the so-called “Aerosil” method. The production temperatures lie between 1000 and 2500 °C (see Figure 3-43.

Along with pure silicic acid, other nanoscale pyrogenic oxides can also be produced with this method, such as aluminum oxide, titanium oxide, zirconium oxide, and mixed oxide or doped materials. After-treatment methods are available for these hydrophilic products, through which the materials can also be hydrophobic. The structure of the produced pyrogenic oxide is pictured in Figure 3-44. One must differentiate between

- the primary particle size, that lies in the lower nm range,
- the aggregate size with values clearly over 100 nm, and
- the agglomerate size.

In the case of the aggregates, it pertains to primary particles that have been baked together, which are bonded together by sintering necks. The agglomerate presents loose collectivizations of aggregates.

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**Figure 3-43: Schematic presentation of an “Aerosil” flame** \[63\]
Differing types of “Aerosil” are distinguishable according to the primary particle size distribution and the specific surfaces (see example of a TEM-photograph in Figure 3-45). The average primary particle size fluctuates between 7 nm with “Aerosil” 300, or 380 and 40 nm with “Aerosil” OX50. The specific surfaces for these products are 300, 380 or 50 m$^2$/g.

“Aerosil” has a wide application range, for example for rheology control in silicones, paints, lacquers, resins, etc., or the usage of pyrogenic oxide as a “flow-aid”. The improved pourability of sugar, salt, and instant cappuccino, and even of extinguishing powder in fire extinguishers or in ketchup for the adjustment to the thixotropy are examples of application [64–65]. Contingent upon the production method, one does not get finely distributed nanoparticles from the “Aerosil” method, but instead agglomerates. Along with nanoparticle production methods from the gas phase, the chemical precipitation and the sol-gel-method are particularly suited for synthesizing nanoparticles in the liquid phase.

### 3.5.1.4 Bottom-up: chemical precipitation

The precipitation of solid materials is a widespread technique for the production of fine particles. The process is generally conducted in an aqueous or non-aqueous solution, which contains the dissolved metal salts. Through the addition of reducing agents, many seed crystals are created, and their growth is controlled mainly by diffusion. The concentration of reagents as well as the temperature play an important role in the production of nanoparticles.
monodisperse nanoparticles. The particle size and the particle size distribution can be controlled by varying the conditions (for example temperature and pH-value). A schematic presentation of a precipitation is shown in Figure 3-46.

The nanoparticles exhibit a highly active surface, which possesses a very high free surface-energy, that must somehow be stabilized in order to prevent agglomeration. By means of chemical precipitation, particles can be generated, such as insoluble salts or oxides and metals with differing forms, such as nanoprisms, nanocubes, nanorods, nanowires etc. The sol-gel-process offers a further possibility for the production from the liquid phase.

3.5.1.5 Bottom-up: sol-gel-process

During the sol-gel-process, metal-chlorides or -alkoxides are hydrolyzed, which causes the products to condense into nanoparticles. Typical sol-gel-reactions are, for example, the production of nanoparticles in the Stöber-process, which have also been discussed in Chapter Figure 3-46. To differentiate: For chemical precipitation, poorly soluble metal-oxides or hydroxides are precipitated from dissolved metal salts by an abrupt change in the pH-level, usually done by adding a strong base. Both reactions can occur in micelles of an emulsion, in which case one speaks of a microemulsion method.

3.5.1.6 Bottom-up: microemulsion method

With this method, precipitation or sol-gel-reactions are performed in emulsion drops instead of a one-phase solution. For the production of nanoparticles the individual emulsion drops are also called “nano-reactors”. The advantage of the micro-emulsion method compared to the one-phase reaction is that only a limited amount of water (namely the amount in the micelle) is available for the respective reaction, by means of which the reaction is more easily controlled. The nano-reactors can either be drops of oil in water, or also water drops in oil (inverse micelles), as schematically presented in Figure 3-47.
With the microemulsion method, the reactants are found in the emulsion drops. The reaction in the emulsion drops is initiated by an extraneous influence, such as a change in the pH-level, the permeation of gases (for example NH₃). The particles resulting from the reaction can take on varying sizes, depending on the salt concentration in the drops.

In addition to the methods explained here, there are a number of further possibilities for the production of nanoparticles, which will not be explored within the scope of this book. Basically, stabilization is necessary after the production of the nanoparticles. Once the particles are formed, they tend towards agglomeration. This can be prevented by an appropriate surface modification.

### 3.5.2 Surface modification of nanoparticles

In order to integrate metal oxide particles homogeneously into a bonding agent, stabilization (as agglomerate-free as possible) is necessary, for example in the form of a stable suspension. A stable suspension is defined as a system consisting of a solid and a liquid phase, in which the solid phase is, composed of individual particles which are in Brownian motion and which retain this condition unchanged [66]. In order to maintain this condition, the individual particles must be protected from an agglomeration.

#### 3.5.2.1 Stabilization of Nanoparticles

On ionic nets and nets of covalently linked three-dimensional networks, the atoms lying on the surface are coordinatively unsaturated, and have “free valences”. Structurally opposing atoms, atom groups or ions can be relatively firmly bonded...