

Silica-Nanocomposites

NANOCRYL® – NANOPOX® – NANOPOL®



Because of their special properties, nanocomposites are mainly used in coatings whose characteristics cannot be produced by conventional means or can only be achieved by multiple coats. Silica-nanocomposites are preferred where high scratch and abrasion resistance is needed at the same time as transparency.

Silicon dioxide nanoparticles can be used in the form of liquid composites in many organic matrices in coating materials.

They:

- improve scratch and abrasion resistance
- improve barrier properties
- improve total transparency of the coating
- have no effect on the degree of gloss
- reduce shrinkage during curing
- reduce tension stress during curing
- improve adhesion on substrates with hydroxyl functions

It follows from the above properties that silica nanoparticles are favored in applications which require transparency and/or high abrasion resistance such as high performance coatings or off-shore topcoats.



Manufacture of silica-nanocomposites

Composites can be manufactured from silica nanoparticles and organic resins using a modified sol-gel process. Despite being 50% w/w filled, they are crystal clear.

Starting from water glass (aqueous sodium silicate solution), spherical silica nanoparticles of ca. 20 nm diameter can be cultured in an aqueous environment and their growth stopped by wet-chemical means. These particles then have their surfaces modified to permit stable transfer into an organic matrix.

Depending on the matrix which will surround it, this modification is performed with various agents and can lead to different results according to the polarity of the matrix and silica-nanoparticles.

In the first purification step, practically all free ions are removed. In a second step, after surface modification with a processing matrix, water is separated. In the third step, the processing matrix is replaced by the final matrix.

Silica-nanoparticles obtained in this way, contain, depending on the matrix, up to 50% silica in nanoparticulate form and are stable for at least six months. These products are crystal clear, completely transparent and show no sedimentation.

Free silica-nanoparticles cannot be prepared by this process as, in the absence of a surrounding matrix, they have a ten-

dency to form agglomerates of μm size which cannot be re-dispersed. This would lead to the loss of all the desirable properties of the silica-nanocomposites, such as transparency and scratch and abrasion resistance.

In principle, a large range of different particle sizes can be produced. An average particle diameter of ca. 20 nm has however proved optimum for:

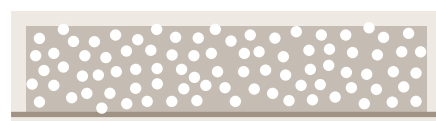
- optical clarity in coating materials
- core/shell ratio
- high amount of silica nanoparticles in the liquid composite
- storage stability

Particle size distribution is very narrow as a result of process optimization.

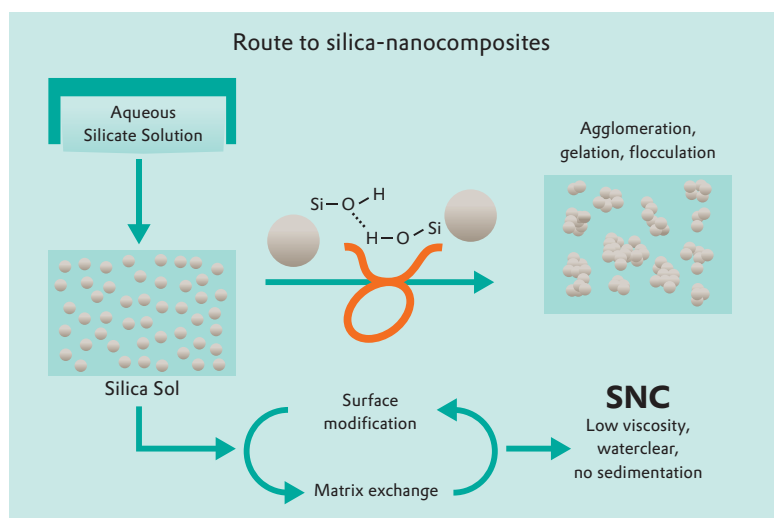
Use of silica-nanocomposites to improve properties

In addition to the main property of scratch and abrasion resistance while maintaining transparency, secondary properties such as barrier effects or reduced shrinkage during curing can also be found in important applications.

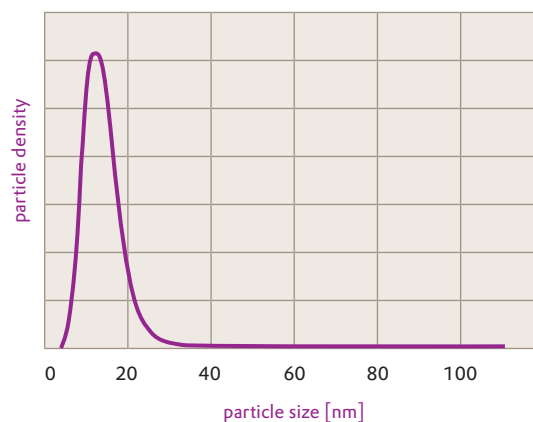
The particles in the cured film are statistically distributed. The distribution is, on average, identical at the surface, in the middle and at the bottom.



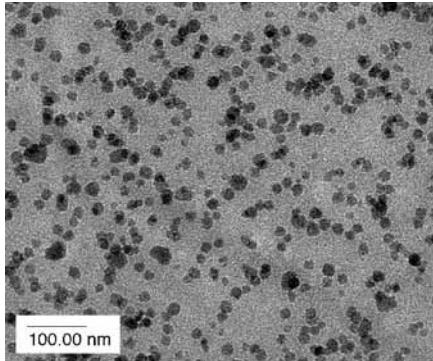
Particle size distribution



Silica phase

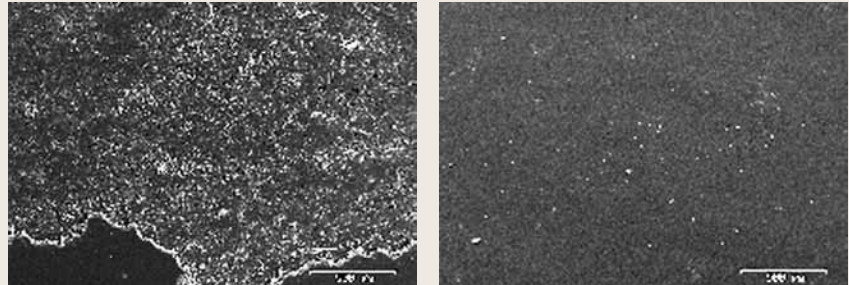


The silica phase consists of discrete nanospheres ($\varnothing$ 20 nm) with an extremely narrow particle size distribution



TEM photo of nanoparticles

Silica-nanocomposites provides steel wool resistance



Microscopic images of cured PPTTA (left) and NANOCRYL® C 165 (50% SiO₂, right) after steel wool scratching

This is quite different from surface active products such as waxes or silicone oils which are only effective at the paint/air interface. Therefore, they only have a temporary effect on the scratch and abrasion resistance and provide protection only over a few load cycles. Current recommendations are for added amounts in the region of 0.5%, as higher quantities can lead to surface defects and incompatibilities.

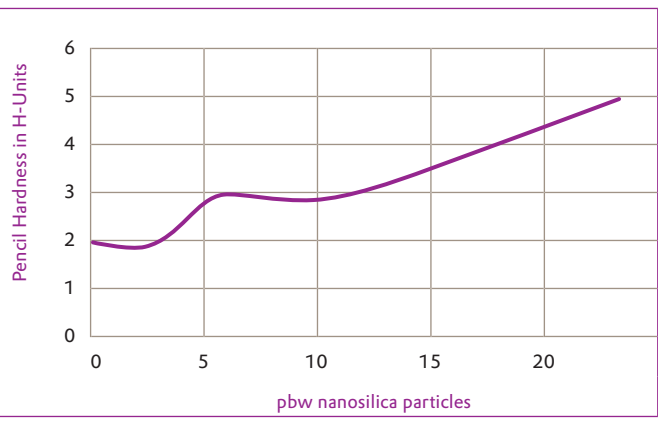
In contrast, silica-nanocomposites offer permanent protection because they are firmly bound into the cured film matrix. Because they are distributed throughout the whole film, the initial recommendation is 5 to 10% w/w relative to the solids of the paint formulation. This amount greatly improves hardness, scratch and abrasion resistance in many applications.

The resistance to abrasion with steel wool is shown for two PPTTA-based coatings – the coating on the right contains 50% nanoparticles and that on the left has no

additive. Both coatings were subjected to rubbing with commercial steel wool and then viewed microscopically. The left sample, which contains no nanoparticles, has sustained heavy damage. In contrast, the sample on the right containing silica-nanoparticles remains undamaged.

Addition of inorganic nanoparticles can alleviate shrinkage during curing. This is important for coating substrates which should not undergo any dimensional change during crosslinking (e.g., warping or distortion of panels, foil or filigrain components).

Relationship pbw nanosilica/pencil hardness



The correct choice of low-shrinkage binders on the one hand and addition of nanosilica on the other is crucial for successful formulation of clear coats. During curing, the nanoparticles achieve an even distribution of forces. Furthermore, introduction of inorganic components in amounts related to that of the shrinkable organic resins leads to smaller effects at the same film thickness.

Similarly, the so-called bending or curling effect which can occur with foils or end-less products is significantly reduced by silica nanoparticles.

As a result of the special surface modification of the nanosilica particles, the silica-nanocomposites only produce a relatively small increase in viscosity. In general,

incorporation of 50% w/w nanosilica leads to a viscosity only four times higher than with the original resin.

The reason for this low increase in viscosity lies in the monodispersed silica nanoparticles which, with their special surface modification, show different behavior to, e.g., milled silicon dioxide or fumed silica. The latter gives rise to an almost exponential increase in viscosity at higher amounts which, at these levels, would lead to a solid mass.

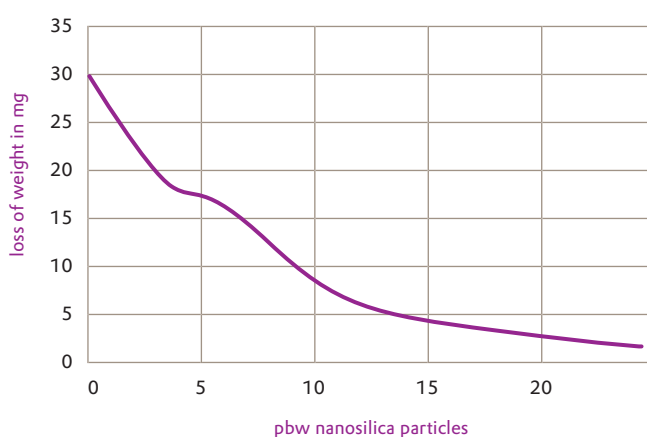
On substrates, such as glass and aluminum, the glassy nanoparticles facilitate adhesion since similar substances adhere well to each other. This effect is exploited in, for example, printing on high quality glass bottles. The demands made on scratch

and abrasion resistance and chemical resistance of print in the cosmetics sector or on bottles for high quality spirits have grown enormously, so that the use of silica nanoparticles can be advantageous.

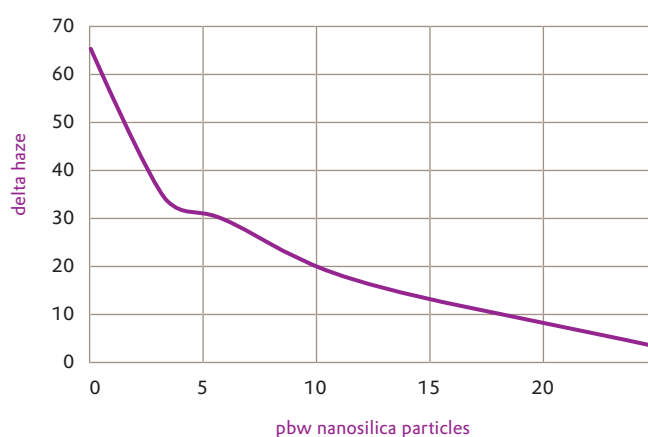
Silica nanoparticles are also suitable for applications where a barrier effect is required especially where transparency is also essential. The barrier effect in an organic transparent coating is increased by the inorganic silica particles. Diffusion of oxygen and water vapor is thus significantly lower than in an unmodified clearcoat.

The addition of silica nanoparticles also generates a barrier effect in the cured film against solvents and can increase resistance by up to 400%.

Relationship pbw nanosilica/loss of weight



Relationship pbw nanosilica/haze



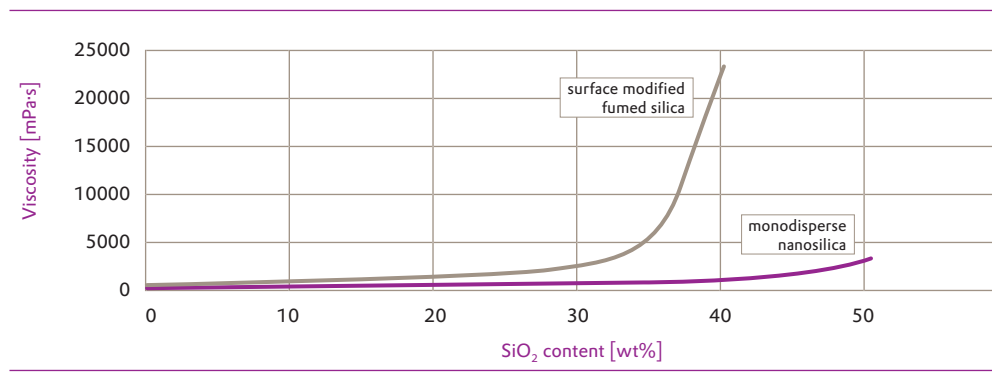


In filler formulations containing microscale fillers or pigments, the nanoparticles can reduce settling of the fillers. This can be attributed to the loosening effect of the nanoparticles which position themselves between the microparticles and prevent close particle packing.

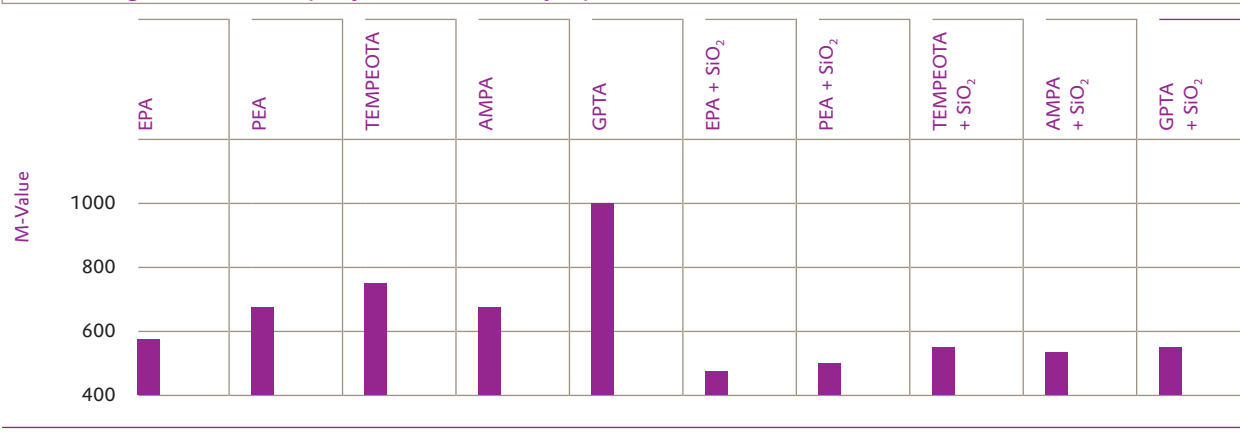
In the cured, filled coating, the nanoparticles can position themselves in the gaps between the filler and the pigment permitting, on the one hand, a marked increase in the absolute filler content (of particular interest for high solids coatings) and, on the other, denser packing of all inorganic components.

The slight increase in viscosity caused by the nanoparticles also plays a part. The reduction of emissions by adding the particles as an extender in formulations is also worth mentioning.

Viscosity build-up of different SiO_2 particles in PPTTA



Solvent migration via ERA (evaporation rate analysis)



The degree of gloss of the formulation is not affected by the silica nanoparticles. Unlike surface waxes or pyrogenic silicas, which are added as matting agents, the nanoparticles do not settle out on the surface but are, as already described, distributed statistically throughout the entire

film. Increased hardness, scratch and abrasion resistance can thus be achieved in coatings of all degrees of gloss.

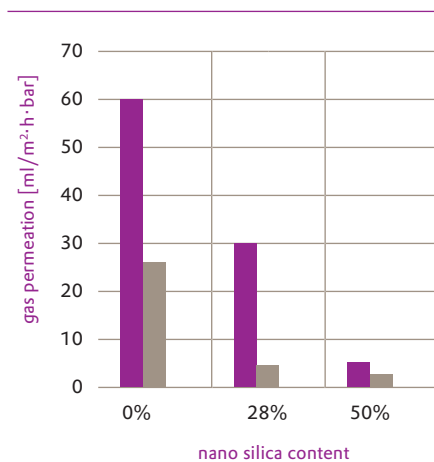
Use of silica-nanocomposites

Incorporation of the liquid composites is easy. Like standard binders, the products are thoroughly stirred together with the main binder at the start of the production process. Dispersing or bead milling is unnecessary. Non-polar resins, solvents or additives are especially unsuitable as they cause the silica nanoparticles to agglomerate or precipitate.

In general, aromatic polyisocyanates (TDI-based) are unsuitable as they rapidly lead to agglomeration, even when used in small amounts or in blends with aliphatic or cycloaliphatic polyisocyanates. Suitable alternatives are aliphatic and cycloaliphatic polyisocyanates such as VESTANAT® T1890.

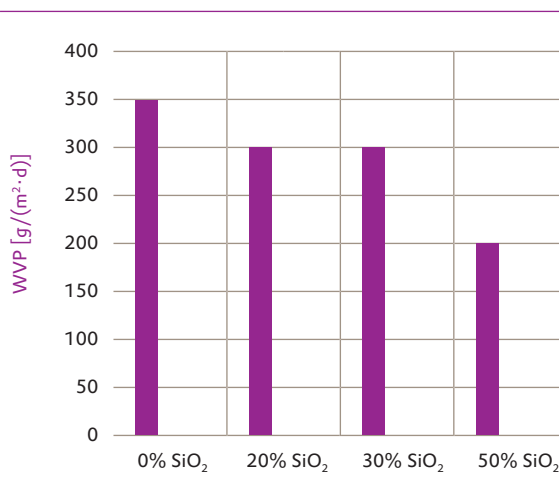


Permeabilities of N₂ and O₂ (DIN 53380)



■ Nitrogen ■ Oxygen
PPTA-Film (20 µm) on PET-Foil (75 µm)

Water vapor permeability (DIN EN ISO 7783-2)



PPTA-Film (45 µm) on cardboard

Amino-functional resins, such as amine synergists for radical-curing UV coatings or aminoplastics for 1-pack stoving enamels, are mostly unsuitable. Compatibility should, of course, always be checked in the laboratory.

Moderately polar solvents such as xylene or toluene should not be used alone in formulations. These solvents are, however, in general very compatible when used in blends with popular solvents such as esters, ketones and alcohols.

Certain additives can result in incompatibilities with silica-nanocomposites. These manifest themselves in, for example, agglomeration, flocculation or increased viscosity of the coating formulation.

Since the times at which such events manifest themselves may be very different, storage tests at raised temperature, e.g. 50°C are recommended:

- to simulate storage at elevated temperature
- to specify a shelf-life (using the Arrhenius principle that reaction rates roughly double for a 10 °C increase in temperature).

To save laboratory time when developing coatings with silica-nanocomposites, compatibility lists are available on request for the additives most commonly used with NANOCRYL®, NANOPOX® and NANOPOL®.

These lists give reliable recommendations for the compatibility of additives with the silica-nanocomposites in terms of short- and long-term shelf-life.

For markedly improved scratch and abrasion resistance, approx 5 to 10% nanoparticles by weight of the solids in a formulation are required – this corresponds to 20% NANOCRYL® and NANOPOL® or 25% NANOPOX® because the silica nanoparticle content differs depending on the form supplied.

NANOCRYL®: products for UV-coatings

Type	Monomer	Characterization	SiO ₂ content [wt%]	Dyn. viscosity, 25°C
NANOCRYL® C 350	HEMA	Hydroxy ethyl methacrylate	50	60 mPa·s
NANOCRYL® C 130	CTFA	Trimethylol propane formalacrylate	50	275 mPa·s
NANOCRYL® C 140	HDDA	Hexanediol diacrylate	50	175 mPa·s
NANOCRYL® C 145	TPGDA	Tripropylen glycol diacrylate	50	200 mPa·s
NANOCRYL® C 150	TMPTA	Trimethylol propane triacrylate	50	3,3 Pa·s
NANOCRYL® C 153	TMPEOTA	Ethox. Trimethylol propane triacrylate	50	1,0 Pa·s
NANOCRYL® C 155	GPTA	Propox. Glycerine triacrylate	50	1,75 Pa·s
NANOCRYL® C 165	PPTTA	Alkox. Pentaerythritol tetraacrylate	50	2,5 Pa·s

NANOPOX®: products for coatings

Type	SiO ₂ content [wt%]	Base resin	EEW [g/equiv.]	Dyn. viscosity, 25°C [mPa·s]	Characterization
NANOPOX® C 450	40	DGEBA	295	60	aromatic
NANOPOX® C 460	40	DGEBA/DGEBF	290	45	aromatic, cristallizationfree

NANOPOX®: product for UV-coatings

Type	Monomer	Characterization	SiO ₂ content [wt%]	Dyn. viscosity, 25°C
NANOPOX® C 620	EEC	Cycloaliphatic epoxy resin for cationic curing	40	4,0 Pa·s

NANOPOL®: products for coatings

Type	Solvent	Characterization	SiO ₂ content [wt%]	Dyn. viscosity, 25°C
NANOPOL® C 764	MPA	Methoxypropylacetate	50	< 50 mPa·s
NANOPOL® C 784	n-BA	N-Butylacetate	50	< 50 mPa·s



Silica-nanocomposites for various coatings systems

Customized silica-nanocomposites for each resin matrix have been developed for the different curing mechanisms in coatings.

All products are characterized by transparency, low viscosity and easy incorporation to the formulation.

NANOCRYL[®], a range of silica-nanocomposites in various commonly used UV-curable acrylate monomers, has been specially developed for radical-curing UV coatings.

NANOPOX[®] materials are manufactured from epoxide resins and suitable reactive diluents. Some products can be heat-cured anhydrously or room-temperature cured with amines or force cured and some are suitable for cationic UV curing.

NANOPOL[®] is a solvent-based product which is almost universally applicable. It is equally suited for use in 1-pack stoving enamels and in 2-pack PUR or UV coatings.

Other modified products are available on request.