Silicone Resins

SILIKOPHEN® – SILIKOFTAL® – SILIKOPON®

Silicone resins and silicone combination resins

An important reason for the wide application and commercial success of silicone resins are properties such as:

- thermal stability
- weathering resistance
- maintaining elasticity at low temperatures
- low surface tension
- hydrophobicity, surface activity
- release and lubricating properties

These properties make silicone resins and silicone combination resins widely applicable in areas such as impregnation of concrete, high-temperature resistant coatings or weather resistant exterior coatings. These binders are used in the form of solutions, liquid resins and emulsions.

$$\mathrm{Si+R\text{-}Cl} \xrightarrow[\text{catalyst}]{\text{ca. 280°C}} \mathrm{R_xSiCl_{4-x}}$$

Figure 1: Müller-Rochow synthesis

General introduction and manufacture of silicone resins

Silicones are organic silicon compounds known as polyorganosiloxanes. This product group can be defined simply as follows:

- they are polymers
- silicon is directly bonded to carbon
- there is at least one oxygen atom connected to the silicon

The silicones occupy a hybrid position between inorganic and organic compounds, specifically between silicates and organic polymers. The siloxane link (Si-O-Si), also found in silicates, is responsible for the “inorganic” character. The organic properties arise from the direct link between silicon and carbon.

The starting point for manufacturing silicone resins are the chlorosilanes which are obtained on a large scale by the Müller-Rochow synthesis. In this, very pure silicon (>98%) is reacted at 280°C in the presence of catalysts and promoters with chemicals such as methyl chloride or phenyl chloride in a fluidized bed reactor (fig. 1).

Structural units for forming polymeric siloxanes (R: methyl or phenyl groups)

Basis monomer	Functionality in terms of hydrolyzable groups	Structural unit in the polymer	Symbol
SiX_4	tetrafunctional (form spatial structures)	$SiO_{4/2}$	Q
$R\text{-}SiX_3$	trifunctional (form spatial structures)	$RSiO_{3/2}$	T
$R_2\text{-}SiX_2$	difunctional (form chains)	$R_2SiO_{2/2}$	D
$R_3\text{-}SiX$	monofunctional (chain breaking or terminating)	$R_3SiO_{1/2}$	M

Table 1

The composition and number of the structural units and the functional groups on the silicon atom determine the structure, processing, and complex properties of the silicone resins. Table 1 shows the structural elements for forming polyorganosiloxanes.

Silicone resin manufacture by Evonik

Chlorosilanes, the starting materials for silicone resins, are generally reacted with water or alcohols (methanol or ethanol) to produce resin intermediates with molecular weights (MW) between 1,000 and 3,000 g/mol. These have many OH- and/or OR- end-groups and no longer contain chlorine. During hydrolysis/alcoholysis of the silane mixture, a dense network of three-dimensional and cyclic structures is formed. Because of this complexity, precise chemical structural formulas cannot be given. In general, silicones are described in terms of their different substituents and reactive groups (fig. 3).

Various techniques have been developed for further modification of the resin intermediates. All Evonik silicone resins are manufactured using a common reaction scheme. First, resin intermediates with well-defined molecular weight and containing almost exclusively SiOR- rather than SiOH-reactive groups are produced. These are crosslinked further with polyols to produce single phase products with a long shelf life.

Varying the resin intermediates and polyols enables the following series of products to be manufactured:

- "pure" phenyl methyl silicone resins (SILIKOPHEN®) with silicone content of approximately 95%, both solvent-based and as aqueous emulsions
- silicone polyester (SILIKOFTAL®) with silicone content of 30 to 80%
- silicone-epoxide hybrid binders (SILIKOPON®) with silicone content of 50%
- silicone-modified, aqueous polyurethane dispersions (SILIKOPUR®)

Because they also con¬tain only a small amount of an organic com¬ponent, SILIKOPHEN® resins exhibit excellent heat resistance. Figure 4 describes SILIKOPHEN® and SILIKOFTAL® resin manufacture at Evonik.

Crosslinking of SILIKOPHEN® and SILIKOFTAL® silicone resins

Chemical Reactions

In general, only a few chemical reactions are important in the manufacture and curing of silicone resins (fig. 2).

Equations (1) and (2) describe the reaction of chlorosilanes with water and alcohol. They occur only during the manufacture of the resin intermediate. Reactions (3) to (6) take place both during resin manufacture and also during curing. Reactions (4) to (6) are particularly important during manufacture as they lead to an increase in molecular weight.

(1) $SiCl + H_2O$ > $SiOH + HCL$
(2) $SiCl + ROH$ > $SiOR + HCL$
(3) $SiOR + H_2O$ > $SiOH + ROH$
(4) $SiOH + SiOH$ > $SiOSi + H_2O$
(5) $SiOH + SiOR$ > $Si\text{-}O\text{-}Si + ROH$
(6) $SiOR + R'OH$ > $SiOR' + ROH$

R' = polyol residue   R = CH_3, C_2H_5

Figure 2: Chemical reactions

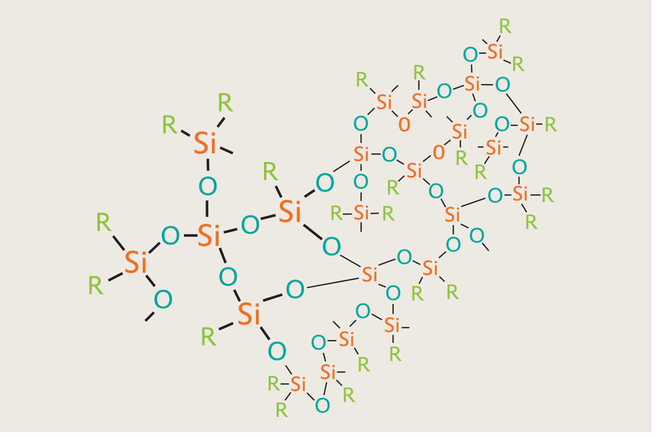


Figure 3: Structure of a silicone resin (idealized, R: methyl or phenyl groups)

The silicone intermediates and organic components such as polyols are not compatible with each other at the beginning of the modification process. They only become compatible and homogenizable as a result of the chemical reactions. The reaction is stopped when the desired molecular weight is reached.

The partially completed modifying reaction (6) is resumed during curing. This involves further reaction of the remaining functional groups in a system which is already strongly crosslinked and for SILIKOPHEN® and SILIKOFTAL® can only occur at high temperatures. Stoving temperatures of at least 200°C are necessary to ensure complete curing.

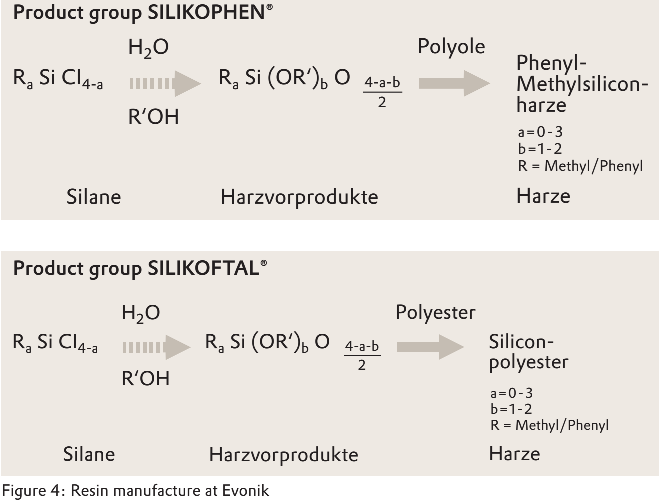


Figure 4: Resin manufacture at Evonik

Crosslinking of silicone resins in the coating

In general, various catalysts only have a limited effect on accelerating the curing reactions of SILIKOPHEN® and SILIKOFTAL® resins. The use of large amounts of catalyst to reduce burn-off temperatures is restricted as problems such as low storage stability, gelling or increased tendency to yellowing can occur. For complete curing without addition of catalyst, we recommend stoving for 30 minutes at an object temperature of 250°C (figure 5 shows the crosslinking reaction of the silicone resins).

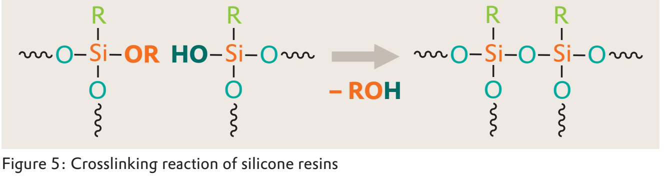


Figure 5: Crosslinking reaction of silicone resins

Applications of silicone resins and silicone combination resins

Guiding formulation for a coating based on SILIKOPHEN® P 80/X with temperature resistance to 500°C

Component	Amount by weight	Ingredient
SILIKOPHEN® P80/X	42.5	Silicone resin
TEGO® Dispers 670	1.0	Dispersing additive
BENTONE® 38	0.3	Rheological additive
Isobutanol	0.5	Alcohol
Butylglycol acetate	1.2	Glycol ester
TEGO® Airex 900	0.5	Deaerator
HEUCODUR® 9-100	6.0	Black pigment
HEUCOPHOS® ZPO	6.0	Corrosion protection pigment
MICA TM	17.0	Mica
AEROSIL® 200	0.5	Pyrogenic silica
Xylene	24.5	Solvent
Total	100.0	

Table 2

Maximum service temperatures of binders

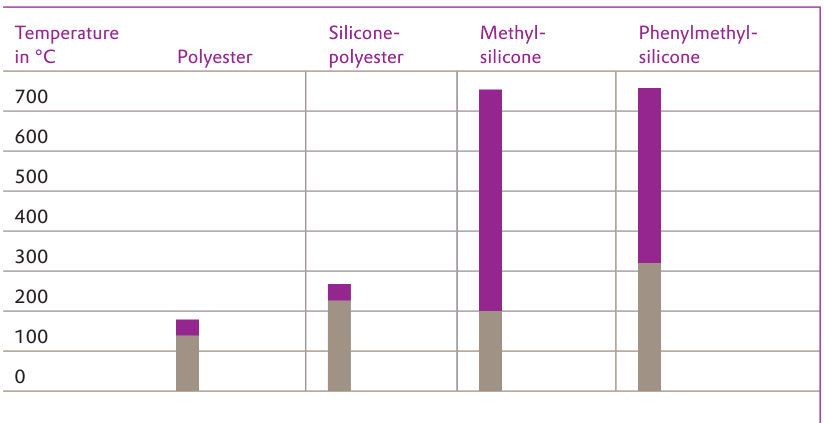


Illustration 1 heat resistance as a function of pigmentation continuous heat resistance

Phenylmethyl silicone resins – SILIKOPHEN® P resins

Evonik offers a range of phenyl methyl silicone resins under the trade name SILIKOPHEN®. The high phenyl group content ensures excellent heat resistance as well as good compatibility with other organic resins. As with all phenylmethyl silicone resin coatings, those based on SILIKOPHEN® P resins are thermoplastic.

Illustration 1 gives an overview of the temperature stability achievable. This depends strongly on the formulation, particularly on the pigmentation. While silicone resins with ethyl or propyl groups have low temperature stability, the heat resistance is distinctly raised if phenyl or methyl groups are incorporated resulting in resins with extraordinary heat resistance up to 350°C.

Such coatings are used mainly in corrosion protection at high temperatures such as car exhausts, smoke stacks, industrial kilns and combustion chambers (fig. 6). The property profile of coatings based on SILIKOPHEN® P resins is strongly dependent on the formulation. For heat resistance up to 350°C, formulations with heat resistant inorganic colored pigments and titanium dioxide are used. The guiding formulations in tables 2 and 3 give examples for long-term temperature levels of 500 and 600°C.

SILIKOPHEN® P resins are characterized by very good pigment wetting. The films remain fully functional even after extended exposure to temperatures of 350°C but may gradually lose their gloss. The maximum thickness of such coatings should (depending on their pigmentation) be less than 25 (±5) µm, otherwise solvent blistering can be caused by alcohol liberated on stoving.

Figure 6: Application of SILIKOPHEN® resins

In addition to this, too high a cured coating thickness looses flexibility when exposed to long-term temperatures over 300°C. Flexibility of such high temperature coatings is obtained by using lamellar fillers such as mica or aluminum flakes. Care must still be taken to ensure the same dry coating thickness as above.

Primers formulated with zinc dust can be used for corrosion-resistant coatings up to 450°C. Coatings which maintain their protective effect up to 600°C are formulated using flake inorganic or metallic pigments such as aluminum and mica (table 3).

At temperatures above 350°C, the organic components of the resin are almost completely burned off. Aided by sintering, inorganic composites are formed which are very hard and completely chemically inert but at the same time very brittle. Burning off organic groups, especially the phenyl substituents of SILIKOPHEN® P resins, leaves microscopically small voids. The resulting matrix system is so flexible that coatings at a temperature of 600°C can be quenched repeatedly with cold water without cracking.

Coatings resistant to temperatures in excess of 700°C can be manufactured using ceramic powders. However, the entire coated surface must be heated above the melting point of the frit. Only then are permanently bonded, enamel-like coatings produced by sintering with the siloxane backbone.

High solid silicone resin SILIKOPHEN® P 80/X or silicone resin emulsion SILIKOPHEN® P 40/W can satisfy demands for a reduction in solvent emission. Table 4 gives a guiding formulation for a waterborne application based on the silicone resin SILIKOPHEN® P 40/W which can withstand continuous use at temperatures up to 500°C.

Guiding formulation for a coating based on SILIKOPHEN® P 80/X with temperature resistance to 600ºC

Component	Amount by weight	Ingredient
SILIKOPHEN® P80/X	52.0	Silicone resin
TEGO® Airex 900	0.5	Deaerator
BLANC FIXE® N	15.0	Filler
AEROSIL® 200	0.5	Pyrogenic silica
STAPA® 4	20.0	Aluminum
Xylene	12.0	Solvent
Total	100.0	

Table 3

Metals such as tin can leach out of metal cans and lead to formation of gel particles. Therefore, manufactured paints should not be stored or packaged in this type of container.

Guiding formulation for a high-temperature resistant coating based on SILIKOPHEN® P 40/W with temperature resistance to 500°C

Component	Amount by weight	Ingredient
Water	26.1	
TEGO® Dispers 750 W	1.5	Dispersing additive
TEGO® Foamex K 3	0.2	Defoamer
Ammonium hydroxide 25%	0.2	Base
HEUCODUR® Schwarz 9-100	8.0	Black pigment
HEUCOSIL® CTF	5.0	Corrosion protection pigment
MICA TM	14.0	Mica
SILIKOPHEN® P40/W	45.0	Silicone resin
Total	100.0	

Table 4

Silicone-polyester resins/ SILIKOFTAL® HT grades

Silicone-polyester resins combine the good properties of silicone resins (temperature resistance, weathering resistance and low surface tension) with those of polyesters (low thermoplasticity, high flexibility and good pigment wetting).

By using thermally-stable polyesters, binders can be produced with a continuous high temperature resistance of 250°C.

With silicone content below 50%, exposure to a temperature of 300°C for three hours produces strong yellowing, typical of an organic resin. With silicone content greater than 50%, the silicone component stabilizes the organic component so that no noticeable yellowing occurs. The probable reason for this is that the higher silicone content increases the inorganic content in the whole polymer thereby decreasing thermal oxidation.

By varying the polyesters and silicone resin intermediates, it is possible to produce silicone-polyester resins with different properties. Evonik offers a wide range of SILIKOFTAL® HT silicone-polyester grades which are customized for specific requirements.

The polyester content ensures good pigment wetting. Thus, for example, white coatings can be produced with gloss values greater than 90 (20° angle). Because of the resistance to yellowing, very light colors can also be formulated.

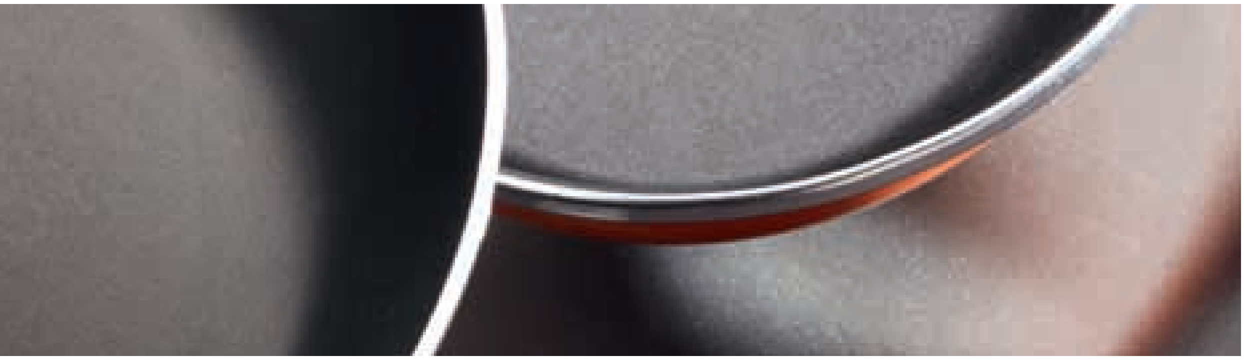


Figure 7: Toaster

Figure 8: Frying pan bottom

A further characteristic of coatings based on SILIKOFTAL® is their low thermoplasticity. As both the silicone and polyester portions are strongly crosslinked, the hardness is maintained even at temperatures around 150°C.

This is important in applications in which the hot coatings are mechanically stressed but must be scratch-resistant.

The properties of SILIKOFTAL® HT grades are particularly advantageous in decorative coatings of thermally stressed appliances such as toasters, tanning beds, fan heaters and cookers as well as the outer coatings of deep fryers, pots and pans (figs. 8 and 9).

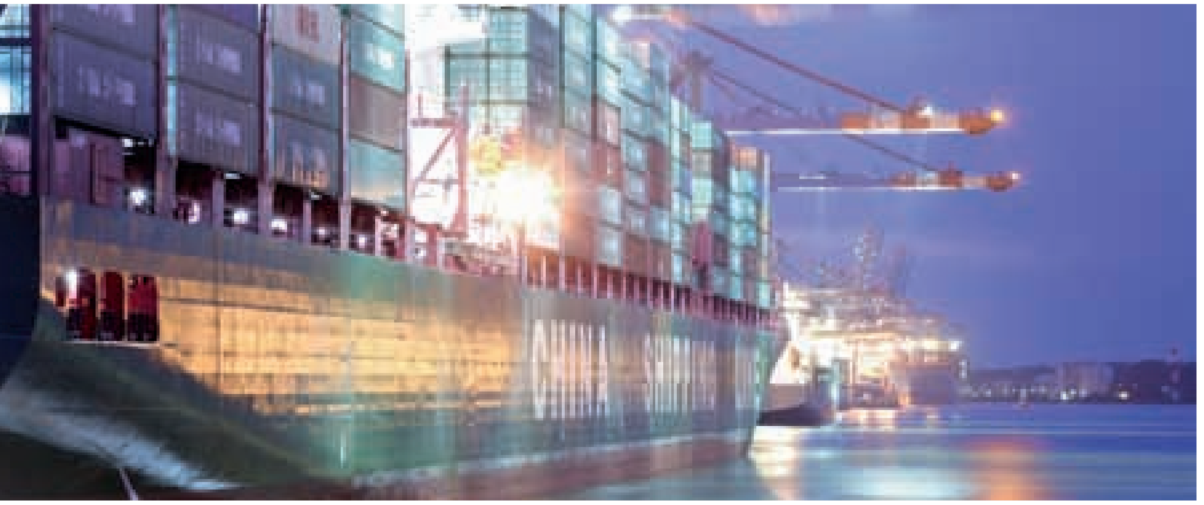
Coatings of some household items must be resistant to detergents so that they can withstand frequent cleaning in a dishwasher without damage using surfactant-containing, strongly-alkaline cleaning agents. Resistance of a coating to detergents is generally determined by the formulation, particularly the binder used. It is an important criteria for the quality of silicone polyesters.

The most important properties of different SILIKOFTAL® HT grades are shown in table 5.

SILIKOFTAL® grades

Product	Silicone content	Properties
SILIKOFTAL® HTT	80%	retains hardness from room temperature to 150°C; long-term heat resistance to 250°C; good detergent resistance. Listed under FDA 175.300 in cured solvent-free resins.
SILIKOFTAL® HTS	70%	very good resistance to yellowing up to 220°C. Listed under FDA 175.300 in cured solvent-free resins.
SILIKOFTAL® HTF	50%	flexible and therefore to a limitedt extent may be deep drawn. Listed under FDA 175.300 in cured solvent-free resins; conforms to BfR.
SILIKOFTAL® HTL	50%	high gloss and low thermoplasticity. Listed under FDA 175.300 in cured solvent-free resins.
SILIKOFTAL® HTL 2	50%	high gloss, low thermoplasticity, good detergent resistance. Listed under FDA 175.300 in cured solvent-free resins.
SILIKOFTAL® HTL 3	30%	very good yellowing resistance up to 200°C, very good boiling water resistance. Listed under FDA 175.300 in cured solvent-free resins; conforms to BfR.

Table 5



Suitable solvents for silicone-polyester resins

In unbaked form, silicone-polyesters still have a high OH-content. These polar groups interact strongly with the ester groups. In the manufacture of the resin, polar solvents are therefore used to inhibit association and thus maintain a stable viscosity. If interactions occur, such as during cooling, these associations only break up slowly upon warming.

There is a time delay in physical properties such as viscosity and conductivity reaching their final value. When formulating coatings, polar solvents such as ketones and esters are preferred to avoid clouding. The use of aliphatic solvents is not recommended.

OH content

The free OH-content of SILIKOFTAL® resins is not specified. When manufacturing these products, the emphasis is on clarity and viscosity rather than constant OH-value.

Stoving conditions and catalysts

In general, the curing reactions of SILIKOFTAL® resins are accelerated by various catalysts. The use of large amounts of catalyst to significantly reduce stoving temperatures is not recommended as it can lead to problems such as poor storage stability, gelling, brittleness and increased tendency to yellowing.

To achieve full curing without addition of catalysts, the following conditions are recommended:

- 60 minutes at 220°C
- 30 minutes at 250°C
- 15 minutes at 280°C

Silicone epoxide combination resins/ SILIKOPON® E grades

The SILIKOPON® range combines the properties of the widely applicable epoxide resins with those of silicone resins. SILIKOPON® EW and SILIKOPON® EC are for high-temperature use. Compared with pure silicone resins (SILIKOPHEN®), these silicone/epoxy hybrids offer better adhesion to metals as well as better corrosion protection and chemical resistance. A typical application is in vehicle exhaust coatings where SILIKOPON® EW or SILIKOPON® EC is used in primers and a SILIKOPHEN® resin in top coats. Such two-coat systems are temperature resistant to 550°C and have excellent corrosion resistance.

Alongside silicone/epoxy hybrid resins for use at high temperatures, SILIKOPON® EF is a further hybrid for use in topcoats in general industrial and maritime applications.

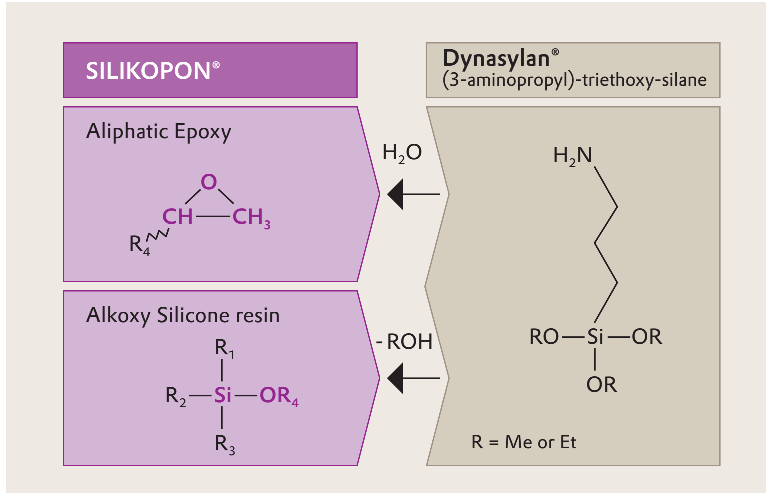


Figure 9: The Dual-Cure Mechanism

SILIKOPON® EF is used as a binder for ultra high solids applications in corrosion protection coatings for steel, coatings for wood and concrete and maritime applications such as biocide-free, easy-to-clean coatings particularly above the water line.

The special feature of the chemical crosslinking of SILIKOPON® EF lies in the dual-cure mechanism at room temperature: the nucleophilic opening of the epoxide ring (by the amine) and the hydrolysis/condensation reaction of the alkoxy groups. Both reactions occur *in situ.* The curing agents are aminosilanes whose amine groups react with the epoxide groups. The three alkoxy groups react in the presence of water or moisture with the free alkoxy group of the silicone resin by hydrolysis/condensation. This "double crosslinking" allows the positive properties of organic and inorganic polymers to be combined in a new class of binders. Because of the high crosslink density (see fig. 9), these coatings have a high dirt-repelling effect and are thus very effective against graffiti.

The hydrolysis/condensation reaction described in figure 9 can be strongly accelerated by catalysts. These can be tin compounds or Lewis acids and illustration 2 shows the reduction in drying time achieved by a tin compound (DOTL) and a Lewis acid (borontrifluoride/ethylamine complex).

This binder is suitable for ultra high solids, eco-friendly coatings. The particular advantage is that it permits production of isocyanate-free, 2-pack formulations with VOC content less than 250 g/l. In the case of, for example, wood clear coats, the VOC can be less than 100 g/l.
The silicone/epoxy resin combination allows two-coat corrosion protection coatings to be manufactured with SILIKOPON® EF which can replace the classic three-coat systems (fig. 10).

Effect of catalysts on the drying of SILIKOPON® EF

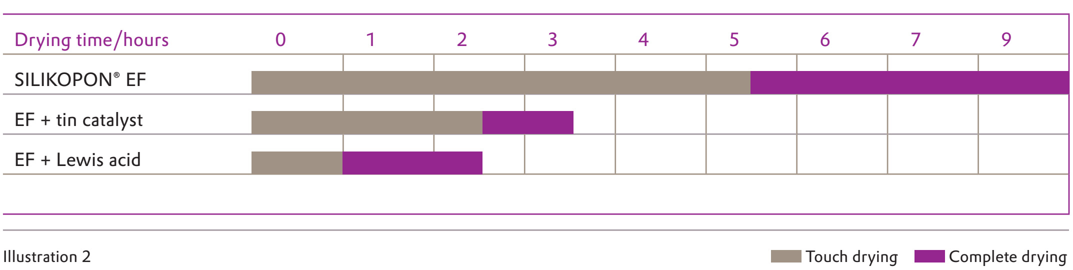


Illustration 2

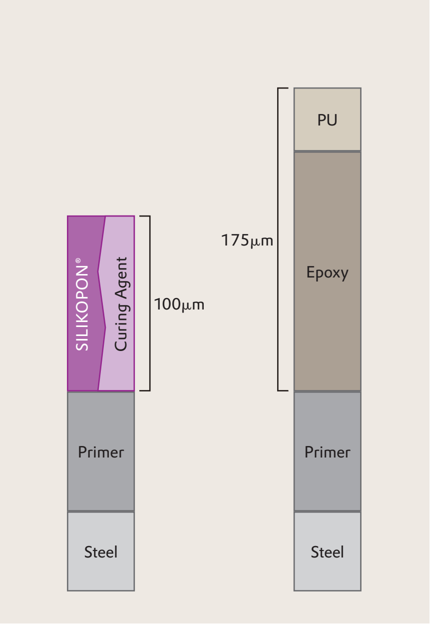


Figure 10: Coating structure

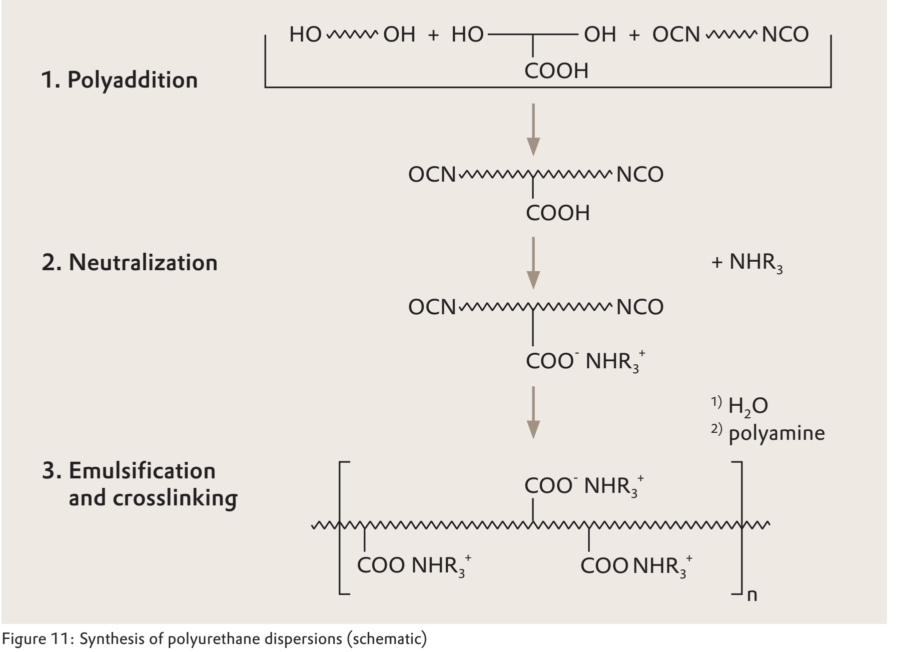


Figure 11: Synthesis of polyurethane dispersions (schematic)

In addition to the reduced coat thickness and hence less material needed, cost savings also accrue because of the reduced time required for coating. Further advantages arising from the high inorganic content are good char resistance and high abrasion resistance. The high crosslinking density of coatings based on SILIKOPON® EF allows this binder to be used in the flooring and industrial plant sectors.

Waterborne silicone-modified polyurethane dispersions

Under the name SILIKOPUR® 8080, Evonik offers a waterborne, N-methylpyrrolidone-free (NMP-free), silicone-modified, 1-pack polyurethane dispersion. This dispersion air-dries at room temperature.

The special properties are as follows:
- quick drying in air
- non-stick effect
- special haptics
- hydrophobic
- high flexibility even at low temperatures (-30°C)
- high elasticity of 300-400%
- good adhesion to flexible substrates
- improved abrasion resistance

Manufacture of SILIKOPUR® 8080

The synthesis of polyurethane dispersions usually occurs as the series of consecutive steps shown in figure 12. A diol, dimethylolpropionic acid and excess isocyanate are reacted together to form an isocyanate-terminated prepolymer. After neutralization and chain extension, it is emulsified in water.

In contrast to this commonly-used synthesis, Evonik largely replaces the polyesterpolyol with a silicone base unit, a dihydroxyalkylpolydimethyl siloxane with two terminal OH groups (fig. 12).

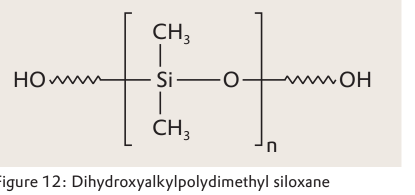


Figure 12: Dihydroxyalkylpolydimethyl siloxane

Applications of SILIKOPUR® 8080

An application of SILIKOPUR® 8080 is the coating of leather in, for example, shoes, clothing or vehicles. The polyurethane formulation increases the slip effect and decreases creaking and squeaking of leather over the long-term.

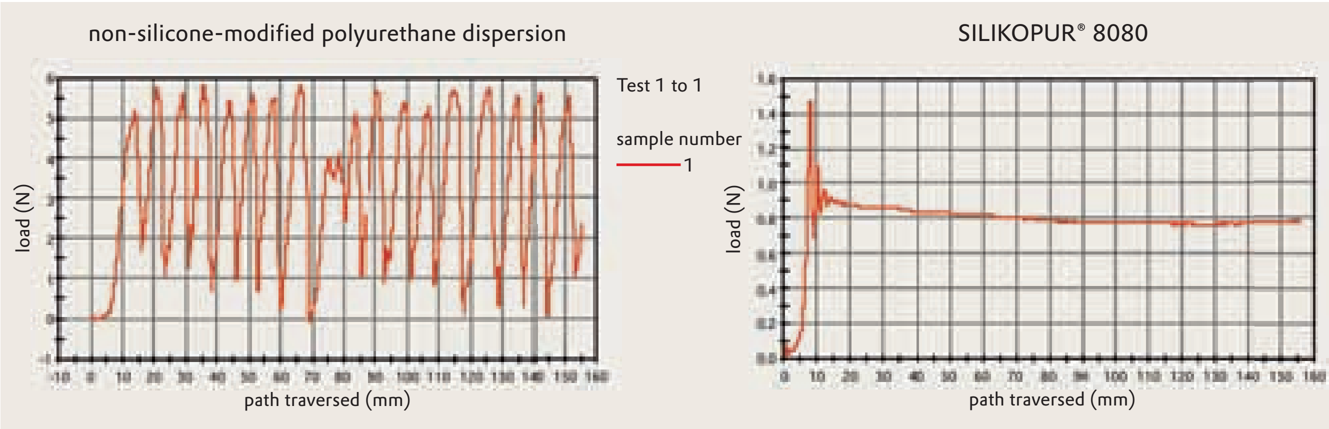


Figure 13: Slip properties

Figure 13 compares the slip properties with those of a usual waterborne polyurethane dispersion.

Because of the silicone modification and the anti-stick properties and high flexibility resulting from it, SILIKOPUR® 8080 is used in release coatings for EPDM. Furthermore, the dispersion has good substrate adhesion properties on many other plastics (ABS, GFP, Nornyl, PA, PMMA, PVC, PC).

Illustration 3 shows that a 30% addition of SILIKOPUR® 8080 as co-binder to an acrylic dispersion can improve abrasion resistance of wood finishes.

Solid and non-volatile components

As with all condensed binders, the amount of solids in SILIKOPHEN®, SILIKOPON® and SILIKOFTAL® is not exactly the same as the amount of non-volatiles. Solids contain low molecular resin components and condensed groups which are not present in the non-volatile residue after drying.

Therefore, the solids content is often a few percent higher than the non-volatiles as determined by DIN 53216. In our data sheets, only the amount of non-volatiles is given as this is the parameter which is important for the user. In contrast, the material safety data sheets give the solids content which is what is important for hazardous goods classification.

Abrasion resistance (CS-17 wheel, 1 kg)

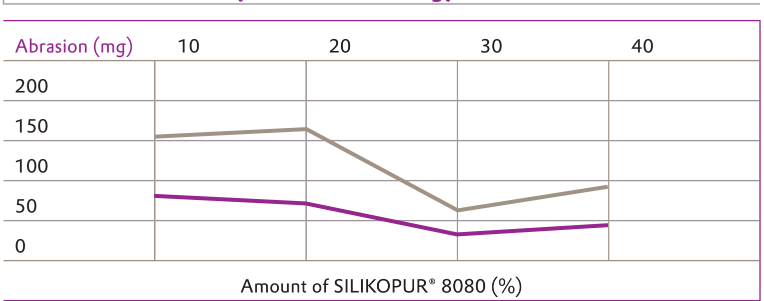


Illustration 3

500 abrasion cycles
1,000 abrasion cycles