

Silicone Resins

SILIKOPHEN®

SILIKOFTAL®

SILIKOPON®

Silicone resins, silicone-polyester- and silicone-epoxide-combination resins

In the Tego Journal the terms silicone, siloxane and similar-sounding chemical compounds appear very frequently. Thus the language itself indicates a strong relationship: silicones and siloxanes are substances which contain, in addition to typical organic constituents such as carbon and hydrogen, silicon, a special inorganic component. In molecules, a silicon atom generally forms bonds to four other atoms. Varying the groups to which the silicon is attached allows a wide range of properties to be achieved, making the compounds suitable for very different areas of application.

Many silicone resins are water-repellent and thus silicones are often used in hydrophobing additives to produce water repelling effects (see "Technical Background: Hydrophobing Agents"). Additionally many of these substances show a good lubricating effect and are therefore used in corresponding additives ("Technical Background: Slip and Flow Additives").

Organo-silicon compounds can also be used to produce silicone resins and different groups of atoms on the molecular backbone allow targeted modification of properties. Silicone resins are characterized by a branched framework of silicon atoms connected with each other by oxygen atoms.

This basic framework of siloxane links gives silicone resins special properties such as high heat and weathering resistance. In this respect silicone resins are quite different from purely organic resins. Silicone resins are firmly established in the binder market both as "pure" silicone resins and also as silicone combination resins such as silicone-polyester resins and silicone-epoxide resins. Specially adapted resins are used for a very wide range of areas of application.

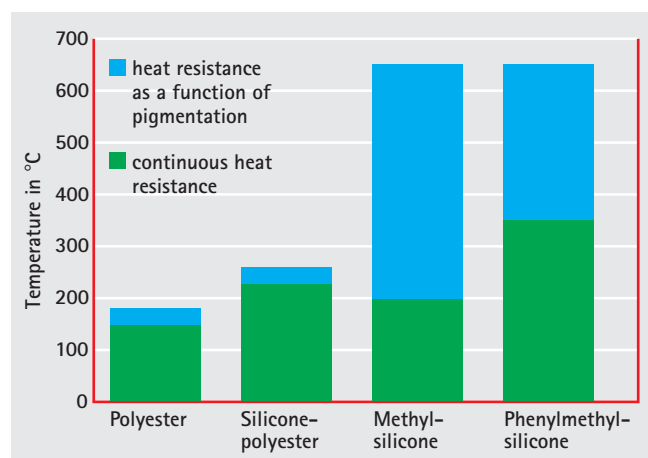
Thus there are resins

- with low surface tension used as release agents
- for corrosion protection under extreme conditions
- for decorative coating of temperature resistant household appliances
- for coatings with high weathering resistance
- for coating highly stressed steel structures in the maritime sector
- to make building materials water repellent

Graphic 1 gives an overview of the heat resistance which can be achieved, although this depends strongly on the formulation, particularly the pigmentation. While silicone resins with long alkyl chains do not withstand high temperatures very well, the heat resistance is markedly raised if the alkyl chains are replaced by phenyl or methyl groups. This results in extraordinarily heat resistant resins stable up to 350 °C. The Tego products described in this chapter belong to this group and have proved themselves effective for corrosion protection at high temperatures.

What is the chemical structure of silicone resins?

Silicon is quadrivalent and the silicone monomers used in the manufacture of silicone resins have four substituents. Of these up to three are organic and the remainder are usually chlorine atoms. To achieve high heat resistance phenyl or methyl substituted silanes are used almost exclusively; in contrast resins



Graphic 1: Maximum service temperatures of resins

used for hydrophobing have longer-chain alkyl groups and have only limited heat resistance.

There is very little interaction between methyl or alkyl silicone resins either with themselves or other organic molecules. Methyl silicone resins are therefore incompatible with other organic resins and are difficult to pigment. In contrast, interactions between the phenyl groups of phenyl methyl silicone resins and other organic materials are much stronger. Phenyl methyl silicone resins can therefore be easily blended with other organic resins (Cold Blends) and are also easy to pigment.

How are silicone resins manufactured?

Chlorosilanes, the starting materials for silicones, are generally reacted with water or alcohols (methanol, ethanol or butanol) to produce resin intermediates with molecular weights of several thousand g/mole. 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 cyclic structures is formed. Because of this complexity, precise chemical structural formulae cannot be given. In general it is sufficient to characterize silicones by their different substituents and reactive groups. Various techniques have been developed for further treatment of the resin intermediates.

All Tego silicone resins are manufactured using a common reaction scheme. First, resin intermediates with well-de-

fined molecular weight and containing almost exclusively SiOR- rather than SiOH- reactive groups are produced. These react further with compounds containing OH-functional groups to produce highly compatible products with an extremely long shelf life.

Varying the siloxane intermediates and polyols enables the following series of products to be manufactured by this scheme:

- silicone polyester (SILIKOFTAL®) with silicone content of 10 to 80%
- "pure" phenylmethyl silicone resins (SILIKOPHEN®) with silicone content of 95%
- silicone-epoxide hybrid binders (SILIKOPON®) with silicone content of 50%

In spite of the fact that they also contain a small amount of an organic component, SILIKOPHEN® resins are just as heat resistant as silicone resins which have no organic component.

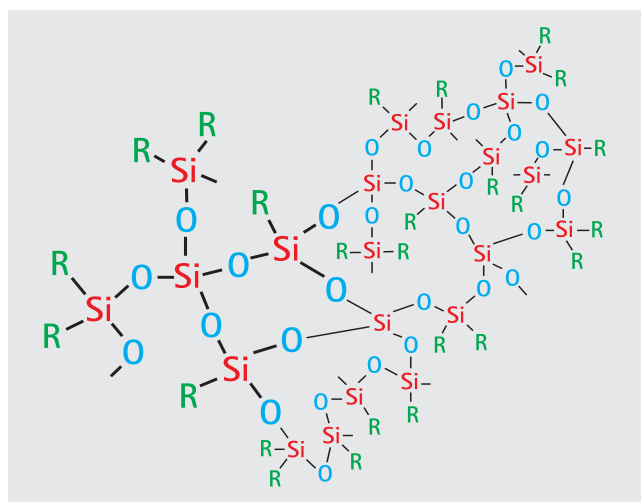


Figure 1:
Silicone resin –
cross-linked

What chemical processes occur in the manufacture and curing of silicone resins?

In general only a few chemical reactions are important in the manufacture and curing of silicone resins.

The first two reactions (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 (5) take place both during resin manufacture and also during curing. Reactions (4) and (5) are particularly important during manufacture as they are related to an increase in molecular weight.

If the desired molecular weight is reached or the resin is completely homogeneous in solvent-free form, the reaction is stopped. This is necessary because the components used are not compatible with each other at the beginning of the modification reaction. Particularly in the manufacture of sili-

cone combination resins the most difficult step is the reaction of incompatible, multi-functional reaction moieties without forming a gel.

The partially completed modifying reaction (5) is resumed during curing. This involves further reaction of the remaining functional groups in a system which is already strongly cross-linked and can only occur at high temperatures. Stoving temperatures of at least 200 °C are necessary to ensure complete curing.

How do the phenylmethyl silicone resins perform?

Degussa offers a range of phenylmethyl silicone resins under the trade name SILIKOPHEN® P. 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.

Such coatings are used mainly in corrosion protection at high temperatures, e.g., car exhausts, smoke stacks, industrial kilns and combustion chambers.

Reactions:

- (1) $\text{SiCl} + \text{H}_2\text{O} > \text{SiOH} + \text{HCl}$
- (2) $\text{SiCl} + \text{ROH} > \text{SiOR} + \text{HCl}$
- (3) $\text{SiOR} + \text{H}_2\text{O} > \text{SiOH} + \text{ROH}$
- (4) $\text{SiOH} + \text{SiOH} > \text{SiOSi} + \text{H}_2\text{O}$
- (5) $\text{SiOR} + \text{R}'\text{OH} > \text{SiOR}' + \text{ROH}$

$\text{R}' = \text{Polyol residue}$ $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$

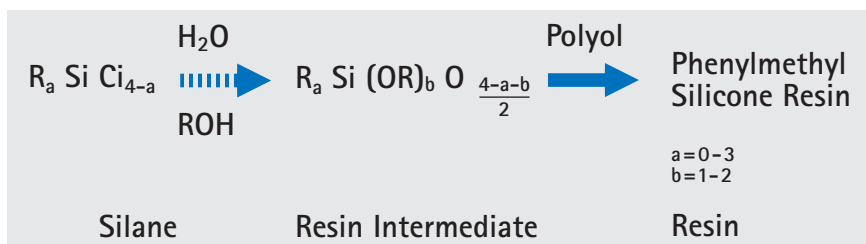


Figure 2 and 3: Resins synthetics at Degussa Tego

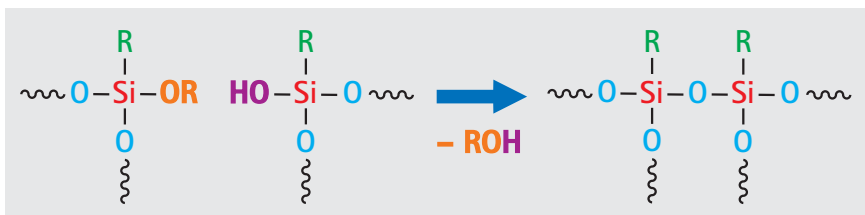
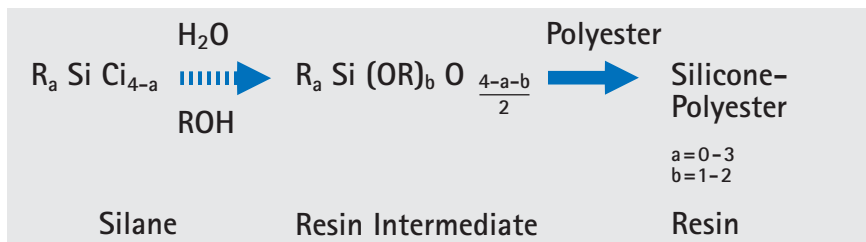


Figure 4: Cross-linking reaction silicone resins

The property profile of coatings based on SILIKOPHEN® P resins is strongly dependent on the formulation. For heat resistance up to 350 °C, clear coats and formulations with heat resistant inorganic colored pigments such as chrome oxide green, cobalt blue, nickel titanate yellow, iron oxide red, spinel black and titanium dioxide are used (fig. 5).

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 gradually lose their gloss. The maximum thickness of such coatings

should (depending on their pigmentation) be less than 40 µm otherwise solvent blistering can be caused by bubbles of alcohol condensation on stoving.





Figure 5: Application for SILIKOPHEN® P resins

Primers formulated with zinc dust can be used for corrosion-resistant coatings up to 450 °C. Coatings which maintain their protective effect up to 650 °C can be formulated using flake inorganic or metallic pigments such as aluminum and mica (fig. 5).

At temperatures above 350 °C the organic component of the resin is almost completely burnt off. Aided by sintering, inorganic composites are formed which are very hard and chemically completely inert but at the same time very brittle. The condensation of the organic groups, especially the phenyl substituted SILIKOPHEN® P resins, leaves 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 (frits). However the entire coated surface must be heated to above the melting point of the frit. Only then are permanently bonded, enamel-like coatings produced by sintering with the siloxane residue.

Mixing with organic binders, such as alkyd resins or acrylate resins (Cold Blends) often enables the property profiles of coatings based on SILIKOPHEN® P resins to be tailored to specific requirements. For example, adhesion and anti-corrosion properties of a partially cured film can be improved. Drying at room temperature can also be favorably influenced by co-binders. Furthermore, co-binders make it possible to produce coatings which are more elastic because

more voids are formed in the silica matrix when burning off the organic components at high temperatures.

Reductions in solvent emission can be achieved with silicone resin emulsion SILIKOPHEN® P 40/W: baked coatings based on these emulsions display the same characteristics as those of solventborne silicone resins.

What should I be aware of when working with silicone resins?

Stoving conditions and catalysts

In general various catalysts only have a limited effect on accelerating the curing reactions of SILIKOPHEN® resins. The use of large amounts of catalyst to reduce burn-off temperatures is restricted as problems such as low storage stability, gelling, embrittlement 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.

Exact information should be taken from the data sheets of individual products. Metals such as tin can leach out of tinplate containers and lead to the formation of gel particles. We therefore recommend that manufactured coatings are not stored or packed in such containers.

How do the silicone-polyester resins of the SILIKOFTAL® HT range perform?

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).



Figure 7: Bakeware



Figure 8: Waffle iron

By using thermally-stable polyesters, binders can be produced with a continuous high temperature resistance of 250°C. This is made clear in fig. 6 which shows the resistance to yellowing of silicone polyesters with different silicone content. 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 components stabilize the organic component so that no noticeable yellowing occurs.

By varying the polyesters and silicone resin intermediates, it is possible to produce silicone/polyester resins with

different properties. Degussa offers a wide range of silicone-polyesters in the SILIKOFTAL® HT silicone-polyester grades which are tailored for specific requirements.

The polyester content ensures good pigment wetting. Thus 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.

A further characteristic of coatings based on SILIKOFTAL® is their low thermoplasticity. As both the silicone and polyester portions are strongly cross-linked 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 coating of high-temperature household appliances such as toasters, sunlamps, fan heaters and cookers as well as the outer coatings of deep fryers, pots and pans.

Figs. 7 and 8 show typical examples of applications. Coatings of some household items must be resistant to detergents so that they can withstand frequent cleaning in a dishwasher using

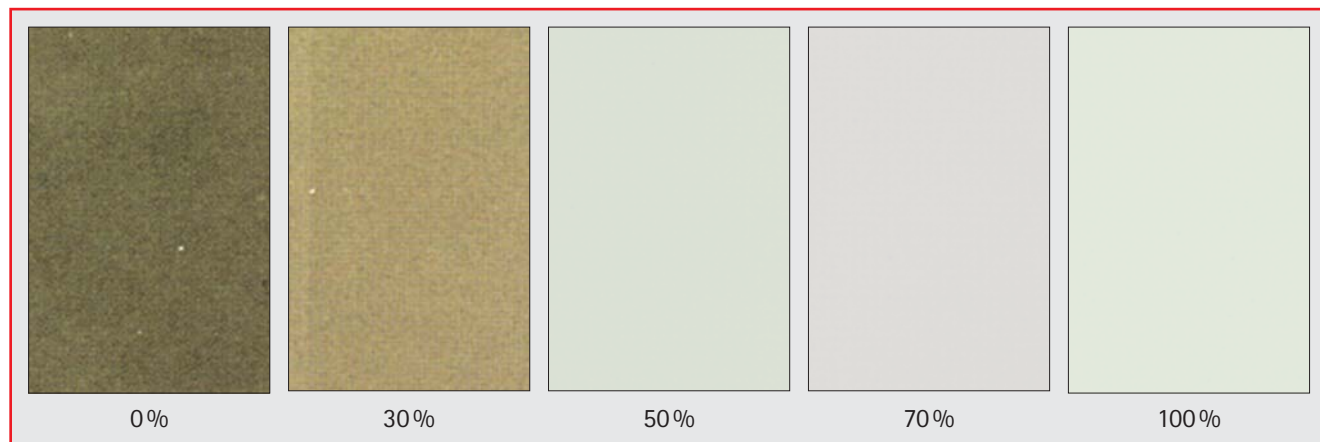


Figure 6: Yellowing resistance of silicone-polyesters

surfactant-containing, strongly-alkaline detergents without damage. Resistance of a coating to detergents is generally determined by the formulation, particularly the binder used. It is an important criterion for the quality of silicone polyesters.

The most important properties of different SILIKOFTAL® HT grades are:

- **HTT** retains hardness from temperature to 150 °C; long-term heat resistance to 250 °C, due to 80% silicone content; complies with BGA. Listed under FDA 175.300
- **HTS** very good resistance to yellowing up to 220 °C. Listed under FDA 175.300
- **HTF** flexible, may be deep drawn. Listed under FDA 175.300
- **HTL** high gloss and low thermoplasticity. Listed under FDA 175.300
- **HTL 2** complies with BGA, high gloss, low thermoplasticity, excellent detergent resistance. Listed under FDA 175.300
- **HTL 3** good yellowing resistance up to 200 °C, excellent boiling water resistance. Listed under FDA 175.300

What are the important things to be aware of when working with silicone-polyester resins?

Solvents for silicone-polyesters

In uncured form silicone-polyesters are polar, because they still have a high OH-content, which interacts strongly with the ester groups. This means that gel permeation chromatography (GPC),

which is usually a very accurate method, can produce values of molecular weights which are too high. In the manufacture of the resin, polar solvents are used to inhibit association and hold the viscosity stable. If interactions occur, e.g. on cooling, these associations only break slowly on warming. Physical properties such as viscosity and conductivity only reach their final value after some time. In formulating coatings the preferred polar solvents are ketones and esters. This avoids clouding. The use of aliphatic solvents is not recommended.

Alcohols can only be used in combination with other solvents. So that the stoichiometry of the stoving reaction is not affected, only highly volatile alcohols can be used. Possible clouding of the binder, following, for example, storage at low temperatures or long standing times, can be eliminated by addition of small amounts of polar solvent. This cloudiness is caused by minute quantities of polyester which did not react in

the modification reaction. Our experience suggests that the quality of coatings is not affected by such clouding.

OH-group content

As with pure silicone resins it is not possible to give an exact figure for the OH-content of SILIKOFTAL® resins.

Stoving conditions and catalysts

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

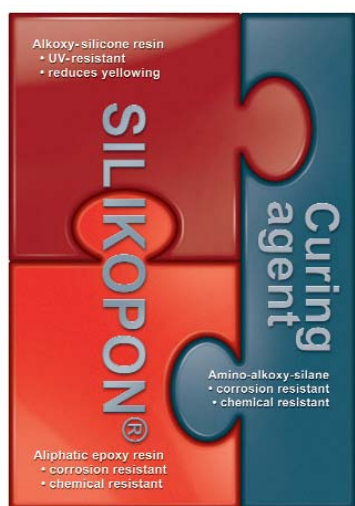
To achieve full curing without addition of catalysts, the following conditions are recommended:

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

Exact values can be obtained from the appropriate product data sheet. Metals such as tin can leach out of metal cans and lead to formation of gel particles and manufactured paints should not be stored or packaged in this type of container.

Solids and non-volatile components

As with all condensation binders, the solids content and the non-volatile content of SILIKOPHEN®, SILIKOPON® and SILIKOFTAL® are not exactly the same. The solids content also includes low molecular weight resin components and condensed groups and is therefore often



2-pack silicone-epoxy-hybrid systems, the best of both worlds

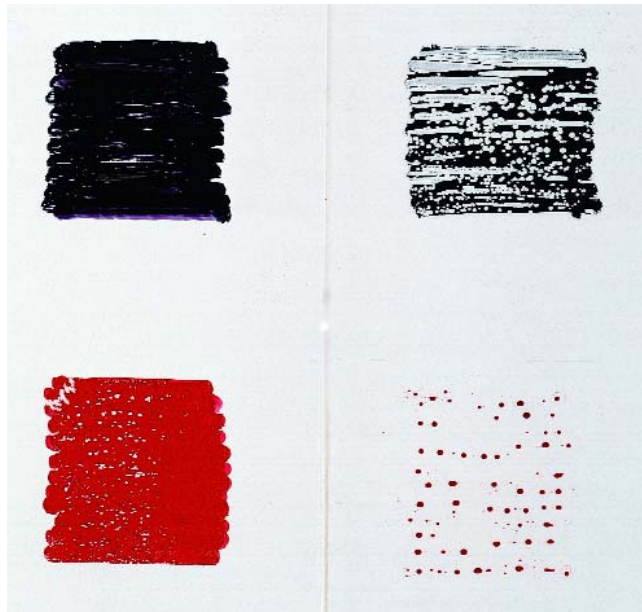
several percent above the value for non-volatiles as determined, for example, to DIN 53216. In our product data sheets only the non-volatile constituents of greatest importance to users are given. The safety data sheets on the other hand give information about the hazard classification of important solids.

How do SILIKOPON® E silicone-epoxide resins perform?

The SILIKOPON® range occupies a special position. SILIKOPON® EW combines the heat resistance of the silicone resins with the good chemical resistance of epoxide resins.

SILIKOPON® EF combines outstanding weathering resistance with high chemical resistance in a 2-pack system. The use of SILIKOPON® EF enables formulation of isocyanate-free coatings with a VOC content below 100 g/l.

High-solids clear coats can also be formulated which, in addition to unique weathering resistance, have "easy-to-clean" and "anti-graffiti" properties (please see clip "Antigraffiti test" on the enclosed CD-ROM).



„easy-to-clean“ properties

