LEARNING BY DOING: SCHOOL EXPERIMENTS WITH WACKER SILICONES

INTELLIGENT INDUSTRY SOLUTIONS

CHEMISTRY MADE EASY– LEARNING BY DOING

WACKER'S EXPERIMENTAL KIT FOR SCIENCE CLASSES

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Silicones – a Polymer climbs the Career Ladder

RELEVANCE TO SYLLABUS AND USE IN THE CLASSROOM

The experimental kit contains a wide range of WACKER products with different properties, so that the proposed experiments and corresponding subject areas have a wide sphere of relevance. The materials presented are aimed primarily at higher-grade pupils. They focus on organic chemistry in daily life, as exemplified by surfactants, paints and plastics.

Many experiments from the field of silicones may be used to cover the subject of polymers. Concepts such as polycondensation and polyaddition can be explained and the background theory underpinned with the aid of experiments involving RTV-1 and RTV-2 silicone rubbers, or the papercoating experiment with DEHESIVE® products.

The structure and various properties (elastomers, viscoelasticity, resistance to solvents) of polymers, particularly silicones, can be readily demonstrated with the aid of the samples supplied (WACKER® BOUNCING PUTTY 29, ELASTOSIL®) and the silicones produced experimentally by the pupils themselves.

The important subject of surfactants (structure and mode of action, use, water pollution etc.) can be readily supported and supplemented by the experiment involving WACKER Antifoam Emulsion SILFOAM® SRE (as well in pulp manufacture). This experiment is also applicable to wastewater purification.

The various experiments on fumed silica (HDK®) can be used for covering the subject of technical silicates and quartz in 10th grade chemistry.

The experiments involving RTV-2 rubbers will help pupils studying catalysis (metastable state, activation energy, catalyst poisons etc.), activation energy (temperature dependence, concentration) and reversible reactions (dynamic equilibrium).

The experiments concerning the thickening of a silicone fluid and the reaction between water and HDK® can be used to demonstrate modifications, intermolecular forces etc. to chemistry pupils.

PREFACE

“One thing is certain: if Germany is to compete successfully with other leading industrial nations, we must earn a top position in the technology sectors of the future. To achieve this, we must particularly encourage the enthusiasm of our country’s young people.” – Dr. Edmund Stoiber, Bavaria’s Minister President, speaking at the International Symposium “100 Years of WACKER Research” on June 23, 2003 at the Technical University of Munich.

Encouraging enthusiasm and maximum performance is a key goal embodied by WACKER’s corporate policy and put into practice every day. For years, the company has actively participated in numerous Bavarian and German projects in order to transfer expertise to schools and universities. In this way WACKER encourages and supports students interested in chemistry.

Silicones, in particular, offer a huge technological and economic potential. They therefore represent a major field of modern chemistry. Yet the teaching curriculum at most usually banishes silicones to the margins of chemistry lessons. That is regrettable, because silicones play a much more important part in our everyday lives than people imagine: silicone rubber under the hood protects vehicle electronics against moisture and dirt. Gloss paints owe their sheen to silicone additives. Silicones in detergents ensure that washing machines do not overflow with foam. Shampoos containing silicones give hair a silky shine. Fire safety cables made from silicones have an outstanding safety record and now even insulators for high-tension cables are being increasingly made from silicone rubber. Silicone resin emulsion paints cause rain water to run off walls while allowing water vapor and carbon dioxide in the underlying masonry to escape. Medical technology, too, abounds with silicones. Because of their compatibility and extreme durability. They are used for medical tubing and for sealing filters in dialysis machines.

WACKER is a member of the chemical industry’s worldwide “Responsible Care” initiative, which aims to raise the credibility of, and faith in, the industry vis-à-vis schools and the public at large. We are making every effort to overcome reservations about chemistry and to establish active, open dialog with schools. The accompanying “experimental kit” is one of our contributions toward this dialog.

We have set ourselves the following goals: to use this experimental kit to help make science lessons stimulating and to increase the accessibility of modern chemistry to teachers and students. Our motto is very much “Learning by doing,“ so the work material we’re putting at your disposal takes account of various German school curriculums.

We have two objectives:
First, the aim is for students to be able to gain the required theoretical and practical knowledge in a stimulating way by experimenting with WACKER’s silicone products and the related explanations. Second, such dialog aims to raise awareness of modern chemistry.

Our experimental kit should also be seen as a teaching aid that can be used in lessons to discuss topics relating to silicon chemistry in a factually in-depth and realistic manner. To supplement the varied work materials, WACKER provides an accompanying booklet that contains focused information and basic theory. When the materials were being prepared, we were mindful of the fact that only minimum supplementary materials and virtually risk-free experiments would be required. The knowledge gained from experimentation can be transferred directly to daily use. The result is both an in-depth and a complementary approach to science lessons.

In the light of the above aims, we trust you will have plenty of fun conducting experiments!

Munich, October 2004

Wacker-Chemie GmbH

SILICONES – A POLYMER CLIMBS THE CAREER LADDER

Silicon: The Basis of Silicones

After oxygen, silicon is the most widespread element on Earth, constituting more than 25 % of the Earth's accessible crust.

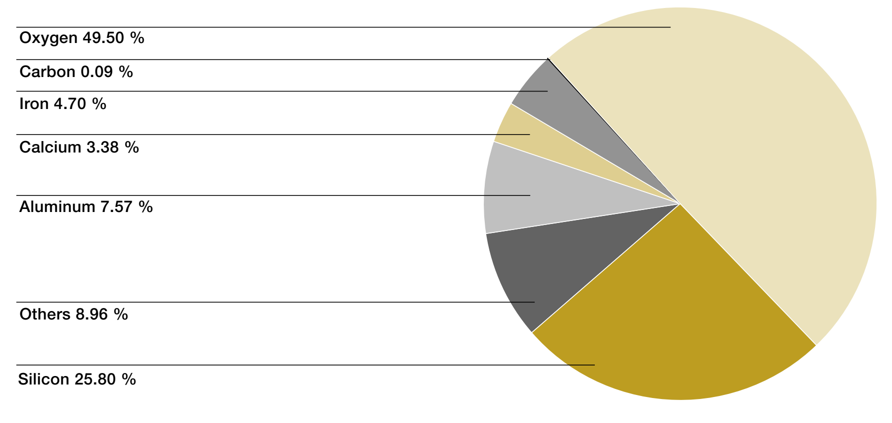
Because it has a high affinity for oxygen, silicon does not occur in elemental form – unlike carbon. Silicon is most often found as compounds of silicic acid, chiefly in the form of magnesium, calcium, iron and mica silicates. Similarly, silicon dioxide is found variously as sand, quartz and gravel. All compounds are based on a tetrahedral structure in which silicon is connected to four oxygen atoms.

Materials containing silicon, such as sand, clay and ceramics, have been in use since ancient times, and were widely available as construction and other working materials. Nowadays, four main forms of silicon are of industrial importance:

- Ferrosilicon and calcium silicide (Ca_xSi_y) as alloying components
- Silicon carbide (SiC) as abrasive and high-performance material (sliding bearings, valves, balls etc.)
- Technical grade silicon (98.5 - 99.7 % Si) in the aluminum industry and silicones industry
- Hyperpure silicon (semiconductor grade silicon)

The number of naturally occurring silicon compounds is minuscule compared with that of carbon compounds. Not even chemical syntheses can compensate for the difference in their respective chemistries.

Distribution of the accessible elements in the Earth's crust



The Manufacture of Silicones

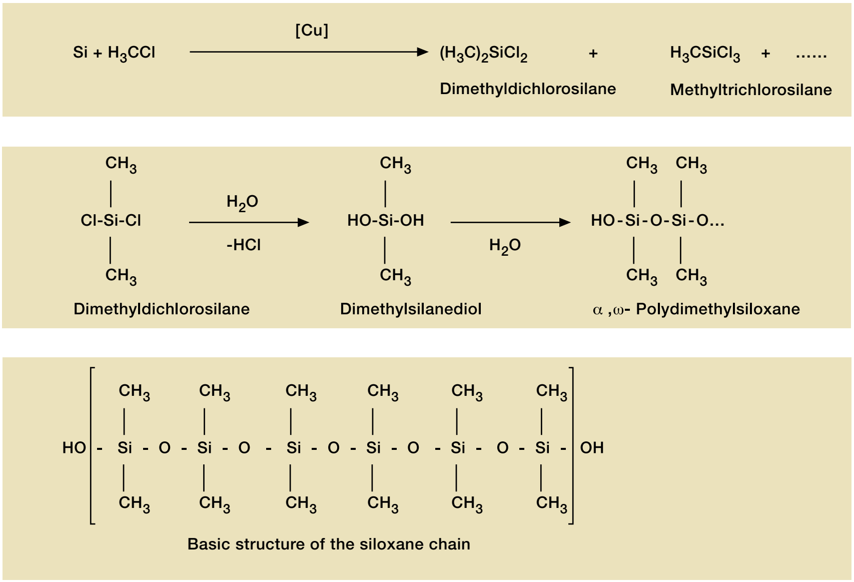
The production of polymeric organosilicon compounds only became economically viable after 1940, when the Müller-Rochow method for the direct synthesis of methylchlorosilanes from elemental silicon was discovered. Methylchlorosilanes are colorless, crystal-clear liquids that are soluble in organic solvents. They are highly volatile because they have a low molecular weight. Methylchlorosilanes are ultimately the starter products for the manufacture of silicones.

The Müller-Rochow synthesis is carried out at temperatures of 250 - 300 °C in the presence of catalytic quantities of copper. The copper is finely ground and then mixed with silicon to make what is known as the contact mass. The synthesis relies on intimate mixing between the contact mass and a stream of methyl chloride. This is best accomplished in fluid-bed reactors. The intimate mixing is necessary for preventing hot spots from forming.

The resultant silanes are then condensed and separated off as liquids. Modern plants are capable of producing more than 70,000 metric tons of crude silane a year with the following composition:

- 85 - 90 % dimethyldichlorosilane $(CH_3)_2SiCl_2$
- 6 - 10 % methyltrichlorosilane CH_3SiCl_3
- 2 - 4 % trimethylchlorosilane $(CH_3)_3SiCl$
- 4 - 6 % polysilanes.

Müller-Rochow synthesis



$$Si + H_3CCl \xrightarrow{[Cu]} (H_3C)_2SiCl_2 + H_3CSiCl_3 + \ldots\ldots$$

$$Cl\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}Cl \xrightarrow[-HCl]{H_2O} HO\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}OH \xrightarrow[H_2O]{} HO\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\ldots$$

$$HO\left[-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-\right]OH$$

Basic structure of the siloxane chain

Reaction equations are not stoichiometrically balanced!

The mixture of liquid crude silanes is separated in a series of distillation columns. Each silane must be very pure because even tiny quantities of mixture will cause chain branching or termination later.

The next reaction stage, hydrolysis or methanolysis, substituents hydroxyl groups for chlorine and liberates hydrogen chloride. The monomers then condense immediately to form a siloxane chain. The type of hydrolysis employed, its underlying mechanism and the composition of the silane mixture determine the chain length of the polysiloxane molecule and the degree to which it is crosslinked.

Conversion into the industrial silicone products is effected through further polycondensation with acidic catalysts at around 130 °C. Addition of chain stoppers, such as $(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$, results in the formation of silicone fluids.

Hydrolysis of trifunctional and tetrafunctional chlorosilanes yields precursors of silicone resins.

Silicones – Materials with Virtually Unlimited Applications

WACKER'S silicones have a wide variety of uses and are supplied as fluids, rubbers and resins.

These three types of silicone are in turn the starting materials for other silicone products, such as greases, release agents, antifoam agents, paint additives, paper-coating agents, hot and cold curing rubber, and water repellents for masonry, textiles and leather.

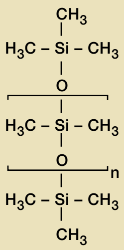
Silicones are a special class of polymer because they not only possess organic properties (due to silicon atoms bonded directly to organic groups) but they are also partly inorganic (by virtue of the siloxane linkage, which is also found in silicates). They could also be described more simply as organically modified quartz. Silicon-oxygen bonds are extremely stable. They have outstanding resistance at extremely high temperatures to UV and IR radiation and to many other influences.

Silicone products are distinguished by the following properties:

- High resistance to heat and cold, ozone and radiation
- Water repellency
- Good release action
- High elasticity
- Good dielectric properties (high insulation performance, good tracking resistance)
- Environmental compatibility
- Physiological tolerance

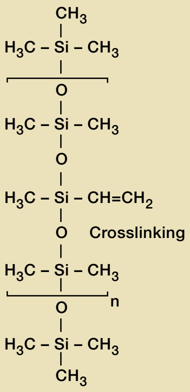
WACKER's silicones have a wide variety of uses

Fluids



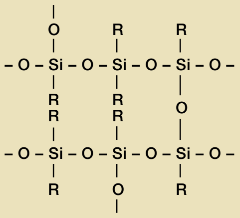
Silicone fluids are linear polymers with chain lengths between two and more than 1,000 Si-O units.
The non-reactive nature of silicone fluids can be modified by incorporating reactive groups or substituents.

Rubbers



Silicone rubbers are based on linear silicone fluids bearing hydroxyl, vinyl or other reactive substituents. The polymers can be crosslinked via these substituents and form wide-mesh structures that are highly elastic.

Resins



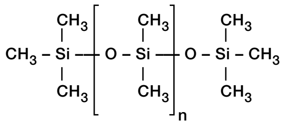
Silicone resins range from relatively low-molecular intermediates to high-molecular, highly crosslinked resins of the most diverse structure.

E1 SILICONE FLUIDS

Chemicals from the experimental kit:
WACKER® SILICONE FLUID AK 1000
WACKER® SILICONE FLUID AK 5000

SILICONE FLUIDS

Basic structure of a polydimethylsiloxane



$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-\left[O-\overset{CH_3}{\underset{CH_3}{Si}}\right]_n-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$

E1.1 Properties and Uses

Silicone fluids are crystal-clear liquids that have no odor or taste. They range in viscosity from 0.65 to roughly 1,000,000 mm^2/s and have unique properties that stem from their molecular structure. Silicone fluids are linear polysiloxanes consisting of alternating silicon and oxygen atoms with unoccupied valences that have been saturated with organic groups. In many respects, the inorganic Si-O bonds are as stable as the bonds in silicates, which are chemically inert. Si-O bonds are therefore much more stable than the C-C bonds of organic polymers.

The silicone fluids which WACKER supplies are called WACKER® SILICONE FLUIDS AK. They are polydimethylsiloxanes with molecular weights ranging from 162 to 74,000 (n = 0 - 1,000). The basic structure is shown in the formula.

The molecular weight, and consequently the viscosity of WACKER® SILICONE FLUIDS AK, is determined by the number of repeating units n in the molecule. In the nomenclature of these silicone fluids, the numeral represents the viscosity of the silicone fluid in mm^2/s at 25 °C. Silicone fluids are liquids over an extremely wide range of molecular weights because their intermolecular forces are weak. They have pour points of around -50 °C, flash points above 300 °C and very low vapor pressures. A particularly striking feature of silicone fluids is that their physical properties, such as viscosity and thermal conductivity, remain fairly constant regardless of temperature change, and that they have good physiological compatibility. Additionally, silicone fluids are insoluble in water.

Reactive organic groups or substituents (e. g. amino or glycol groups) are incorporated into silicone fluids to selectively alter their inertness, and to impart graduated polarity, the latter leading to a wide range of modified properties (copoly-meric silicone fluids and functional silicone fluids). Such modified fluids are notable for their adhesion, and find application, for example, in the treatment of textiles, in cosmetics, and car polishes.

Silicone fluids are also widely used in the form of aqueous emulsions. Emulsions are the best physical form for diluting the fluids with water to achieve homogeneous dispersion when applied in small quantities to substrates (e. g. when used as release agents and impregnating agents). For instance, coating a substrate with a uniform film of a high-viscosity silicone fluid is a difficult task but it is much simpler when an aqueous solution emulsion is used. Emulsions also have the advantage of eliminating the need for organic solvents. This has obvious benefits for industrial health and environmental protection.

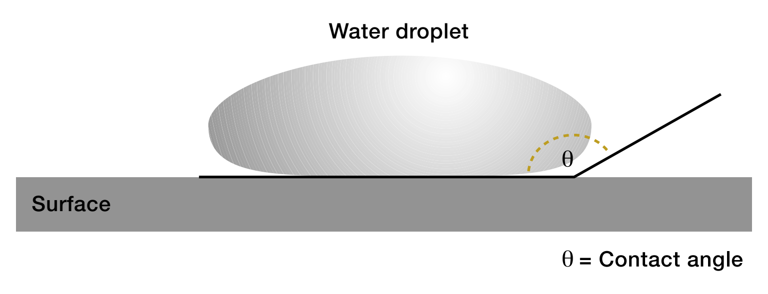
Because of all the properties listed above, silicone fluids and modified silicone fluids are used in a wide variety of applications.

The use of silicone fluids

Purpose	Application area	Properties needed
Releaste agent	Demolding plastic parts, e.g. in the tire industry, fabrication of moldings, etc.	Heat resistance; one thin coat to last for many release processes; prevent the polymers from sticking firmly to the equipment
Lubricant	Plastic bearings, sewing thread, wine corks, cutting tools, film	Reduction in surface friction; ex cellent slip properties; water repellency
Damping medium	Speed regulators, shock absorbing struts, fluid couplings, recording instruments, gyro compasses, nautical and aeronautical instruments	Physical properties remain virtually constant over a wide range of temperatures up to 200 °C
Hydraulic fluid	Shock absorbers, brake cylinders, pumps	Excellent viscosity-temperature response; high compressibility and stability
Liquid dielectric	Coolants, transformers, capacitors, high-voltage tubes, space travel	Radiation resistance; electrical properties remain constant over a wide temperature range
Water-repellent agent	Glass, ceramics, coating materials, switches, insulators, textiles	Low surface tension; high water repellency; hygienic
Antifoam agent	Foam prevention	High effectiveness in very small quantities; odorless and tasteless
In cosmetics	Protective skin creams, sun creams, hair-care agents, insect repellent	Non-toxic; form a water-repellent protective film that allows the skin to breathe and does not irritate it
Polishes additive	Automotive, furniture, floor, and shoe polishes	Gloss retention; water repellency; smoothing effect

E1.2 Silicone Fluids – The Versatile Liquids Experimental Procedure

Contact angle of a drop of water



Experiment 1: Hydrophobic Properties of Silicone Fluids

One way to assess the water repellency of a material is to measure the contact angle, i.e. the angle formed by a drop of water on a surface that has been treated. Contact angles between water and glass or metal surfaces that have been treated with silicone fluids range from 100° to 110°; these values are similar to the contact angle for a surface treated with paraffin. Paraffin is generally considered to be the most hydrophobic material of all.

Uniformly coat one part of a piece of glass, ceramic, metal, paper, etc. with silicone fluid. Then apply a drop of water to both the uncoated and coated parts of each different substrate. What happens? Try repeating this experiment on textiles, such as a paper handkerchief coated on one side with several drops of silicone fluid.

What happens when the drop of water is applied?

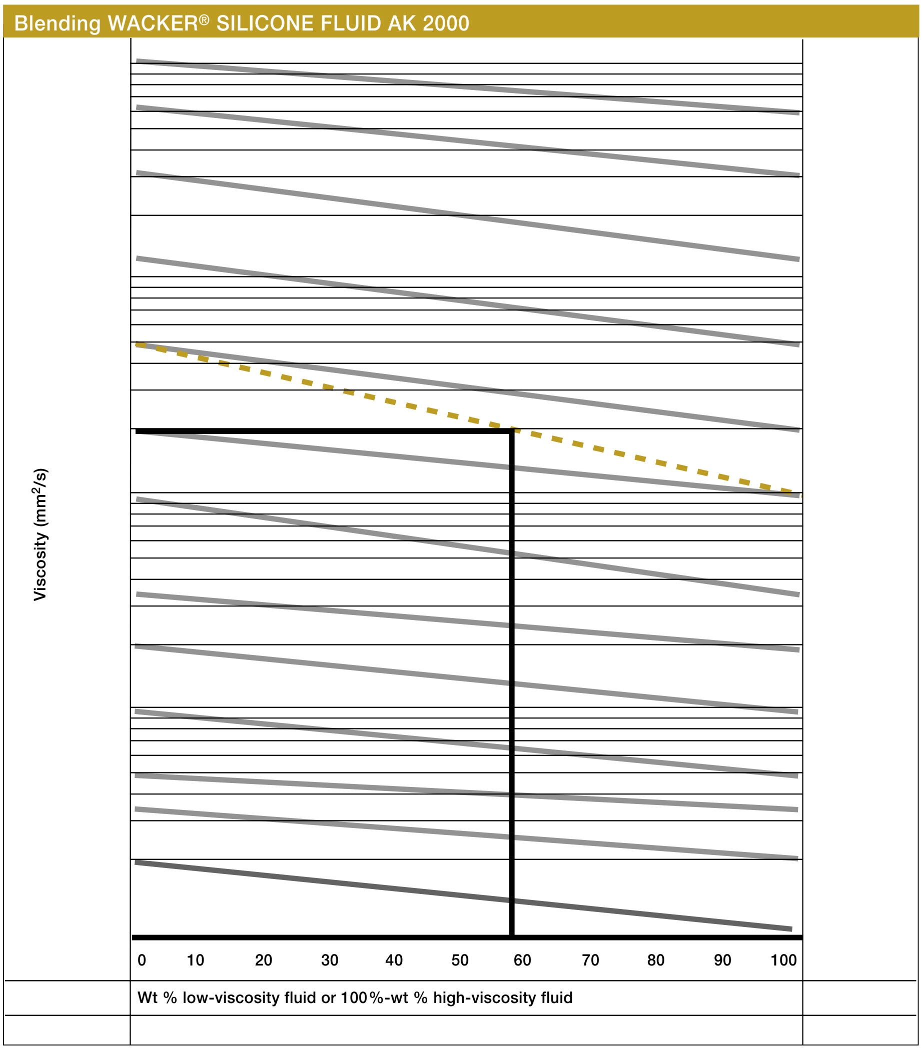
The high water repellency is due to the methyl groups and is most pronounced when a silicone fluid aligns itself on a surface (spontaneous alignment occurs on substrates to which the silicone fluid is attracted, such as glass, building materials, and textiles). Therefore, by combining the hydrophobic properties of the silicone fluid with a suitable primer for the surface concerned, it is possible to produce water-repellent coatings (impregnating agents) that adhere to the surface (see also the experiment on treating building materials with water repellents in Section **E4**).

Experiment 2:
Viscosity of Silicone Fluids

WACKER® SILICONE FLUIDS AK can be produced in a range of graduated viscosities. The precise viscosity is governed by the chain length. Viscosities other than those of the standard grades can be created simply by blending different fluids. Since all the WACKER® SILICONE FLUIDS AK have the same structure, they can be mixed straight away in any ratio. The mixing ratio for producing a given viscosity may be read off from the adjacent diagram. The silicone fluids supplied in the experimental kit can also be mixed to produce any intermediate viscosity.

Creating a silicone fluid by blending:
For example, WACKER® SILICONE FLUID AK 2000 can be obtained from the standard WACKER® SILICONE FLUID AK 1000 and WACKER® SILICONE FLUID AK 5000 supplied by reading off the corresponding weight ratios from the adjacent diagram. To do this, draw a line between 5,000 and 1,000. Then draw a horizontal line from 2,000 to where it intersects with the first line. At the point of intersection, draw a vertical line down to the percentage weight scale.

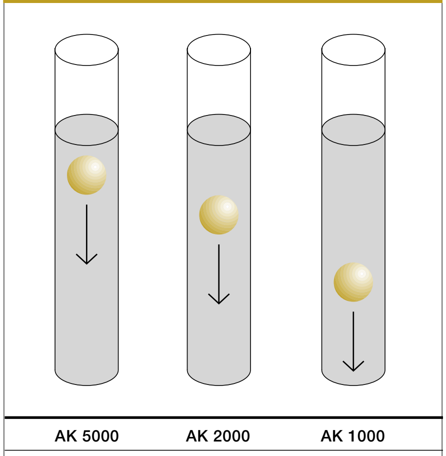
Blending WACKER® SILICONE FLUID AK 2000



Use glass pipets to transfer the various silicone fluids (roughly 20 ml) into identical test tubes. Record the time taken for identical objects to sink to the bottom of each tube. The objects could be metal spheres, or stirrer bars. For comparison purposes, use other liquids, such as water, octane, engine oil, and paraffin oil.

Afterwards, place the test tubes in ice water, a refrigerator or freezer for several minutes and repeat the measurement. Place the test tubes in water at 70 °C for several minutes and repeat the measurement.

Experiments for determining viscosity



Exercise:
Compare the sinking times and interpret these on the basis of type of fluid/liquid, and temperature. Plot the results for the various substances as a graph of temperature against time.

Why the viscosity varies with temperature:
When the temperature of a liquid is increased, energy is added to the system and the mean energy of the individual molecules in the liquid rises. This shows up as faster random movements by the individual molecules (Brownian motion) of the liquid. As a result, the mutual forces of attraction between the molecules in the liquid decrease and the liquid becomes more mobile, i.e. the viscosity falls. The natural logarithm of the viscosity ln η is directly proportional to 1/T.

As with all liquids, the viscosity of WACKER® SILICONE FLUIDS AK varies with changes in temperature, but far less so than in the case of mineral oils, for example. This is why silicone fluids are preferred in applications involving extreme temperatures.

Notes:

E2 HDK® FUMED SILICA – LIGHTER THAN SAND

Chemical from the experimental kit:
HDK® N 20 hydrophilic fumed silica

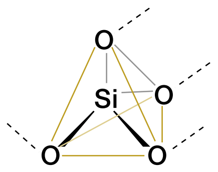
HDK® FUMED SILICA – LIGHTER THAN SAND

E2.1 Formation and Properties

Silica is found almost everywhere in nature, for instance, in the form of gravel and sand. From the point of view of its constituents, fumed silica (HDK®) may therefore be regarded as common sand. One could say, then, that WACKER produces artificial sand – in the order of 15,000 metric tons annually, or about 5,000 truck loads. Why do we take the trouble to make this artificial sand when sand is in such plentiful supply? **The answer** is that this artificial sand has totally different properties than those of common sand.

Production of HDK® starts with feeding volatile chlorosilane (tetrachlorosilane, methylchlorosilanes, etc.) into a hydrogen flame. The high temperatures involved result in in situ formation of water, which hydrolyzes the silane to fumed silica (HDK®) and hydrogen chloride gas:

SiO_4-tetrahedron



The process is closely monitored and contact with the flame is kept short to ensure that spherical primary silica particles with a mean particle size of 5 - 30 nm are formed. One primary particle contains roughly 10,000 SiO_2 units. The primary particles accumulate to form aggregates measuring roughly 100 nm in diameter.

Production at WACKER has the major advantage that the silicas are manufactured together with other silicone products in an integrated production system. Thus, byproducts from other production areas serve as high-grade starter materials for the production of HDK®. The resultant fumed silica is highly pure and has a wide range of service temperatures. Whereas the SiO_4 tetrahedra, the smallest structural elements in sand or quartz, are arranged totally regularly in a three-dimensional crystal lattice, they are randomly dispersed in the primary particles of HDK® to yield an irregular, non-crystalline (amorphous) system without any fixed shape.

When HDK® is added to a liquid, hydrogen bonds are formed between the silanol groups of neighboring silica aggregates. A three-dimensional network builds up that reduces the mobility of the liquid molecules. The denser this network, the higher is the viscosity of the liquid.

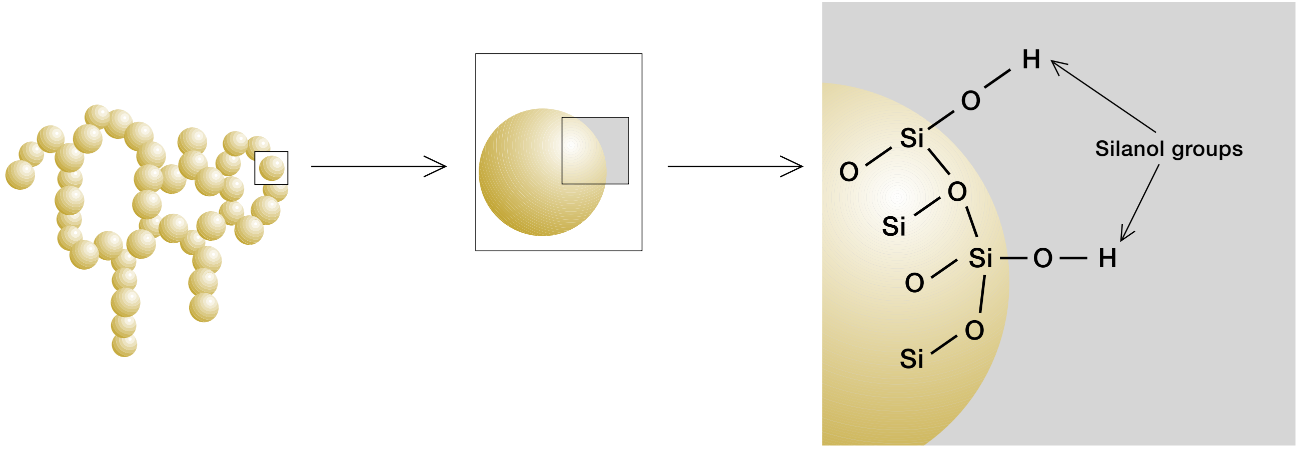
E2.2 Digression: Rheology – The Laws of Liquid Systems

Rheology (from the Greek **rheos** meaning **anything flowing**) is a branch of physics that deals with the flow and deformation of matter, especially liquids. In order for a liquid at rest to move, a force must act on it. This is described by the shear force (shear stress) τ and may be imagined as the displacement or sliding of thin layers of liquid over each other. The velocity with which this displacement occurs is called the shear rate **D**. Dividing τ by **D** yields the dynamic viscosity, η, more often referred to as viscosity:

$$\eta = \frac{\tau}{D} \ [\text{Pa s}]$$

Viscosity is a measure of the extent to which a material resists a force tending to cause it to flow. If the viscosity is ideal, i. e. the viscosity is independent of the shear rate **D**, the liquid is said to be Newtonian. This means that η is a constant at a given temperature. Newtonian flow occurs only in the case of gases, low-molecular pure liquids or solutions and dilute suspensions of spherical particles. Examples are water, gasoline, lubricating oils, and hydraulic liquids.

Structure of HDK® fumed silica



Fumed silica **Primary particles** **Chemical structure of HDK®**

The viscosities of some common liquids are listed in the following table (measured at 25 °C, in mPa s).

Viscosity of some common liquids

Substance	Viscosity [mPa s]
Ether	0.238
Chloroform	0.579
Benzene	0.673
Water	1.002
Ethanol	1.22
Castor oil	1,060
WACKER Silicone fluids	0.65-1,000,000
Glass	10^{17}

Most materials do not exhibit ideal viscosity but instead have the properties of so-called non-Newtonian liquids. In their case, the viscosity is not constant at a given temperature, but is dependent on the shear rate, **D.**

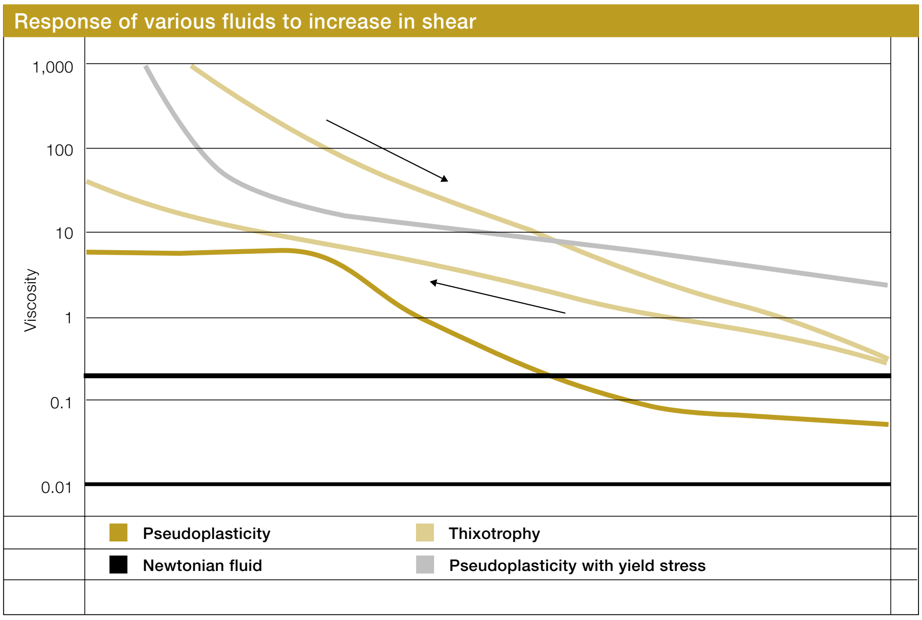
Non-Newtonian liquids play a large role not only in industry (e. g. brine, gels, highly concentrated suspensions, polymers), but also in physiology (blood). Many systems exhibit a strong decrease in viscosity if the shear rate is increased, i. e. the viscosity is changed by the action of movement (stirring, agitation, etc). Such systems are said to be pseudoplastic. Pseudoplastic materials with yield stress are solid under normal conditions and liquefy only under the action of shear stress. Typical examples of such pseudoplastic substances are chocolate, fat, toothpaste, and ointments (see also the diagram on the next page).

While the shear history (i. e. duration of shear) does not affect the viscosity of a pseudoplastic material, it has a major influence on thixotropic systems. A thixotropic system is essentially a pseudoplastic material whose decrease in viscosity under shear is accompanied by a time lag.

Example:
A thixotropic system becomes more fluid the longer it is stirred at a constant velocity.

Thixotropic liquids are produced in vast quantities for the surface coatings industry. Modern, non-drip paints are thixotropic. They can be spread easily and are highly fluid while they are being spread. However, at rest, their viscosity is much greater, and so no running or sagging occurs on the coated surface. In surface coatings and other paints, thixotropy is achieved by adding a so-called thixotrope, e. g. bentonite, kaolinite or, especially, SiO_2 compounds, which are effective at preventing settling. In other systems, thixotropes act as thickeners to change the consistency of food and toiletries. A well-known example of a thixotropic liquid is ketchup.

Response of various fluids to increase in shear



E2.3 Thickening and Thixotropy – Reinforcement – Flow Experimental Procedure

Experiment 1: Comparison of Natural Sand and HDK®

Weigh out 0.1 g HDK® N20 and 0.1 g sand onto filter paper. Compare the volume and the appearance of the two substances. Which differences can you detect with the naked eye or by touching the substances with your fingers?

Production of fumed silica can be modified so as to yield grades with different physicochemical properties. Thus, the specific surface area of the HDK® N20 grades can be varied from 125 to 400 m^2/g. 30 g of HDK® N20 has a surface area the size of a soccer pitch, i.e. 6,000 m^2 (for comparison: the lungs have a surface area of 80 - 120 m^2, equivalent to 0.6 g HDK® N20). If all the primary particles present in 1 g of fumed silica were placed in a line, the line would stretch 17 times to the moon! HDK® therefore has a much much greater surface area than sand. This explains why fumed silicas have so many unusual properties compared with sand.

Experiment 2:
Scattering Power of Salt

Sometimes, no matter how often salt shakers are tapped or shaken, the salt inside refuses to come out. This is because salt absorbs atmospheric moisture. Take 50 g of salt and spray it with 5 milliliters of water. What happens? Now add 3 heaping spoonfuls of HDK® N20 and shake well.
What happens now?

Explanation:
The fumed silica has a high affinity for water and can bind a large amount of water in its interstices.

Experiment 3:
Flow Properties of Sulfur

To 10 g of sulfur in a sealable glass vessel, add 0.1 g (heaped spatula tip) HDK® N20. To a second glass vessel, add just 10 g of sulfur for comparison purposes. Observe the behavior of the sulfur in the two vessels and then as it flows through a wide-neck funnel.

Explanation:
HDK® N20 is an excellent free-flow aid. The tiniest of additions (0.01 - 3 weight percent) is enough to improve the flow properties of powders. What happens is that the poorly flowing solid particles become enveloped in tiny HDK® spheres to produce a ballbearing effect. In addition, the tiny HDK® spheres prevent the powder particles from sticking together and interacting with each other.

Uses:
HDK® as dispersing and grinding aid:
fragments become enveloped in HDK®; this prevents high-energy fracture surfaces from recombining; typically used as an additive in the grinding of sulfur.

HDK® increases the flow capability and storage stability of powders:
HDK® powders are used in fire-extinguishing powders, common salt, in tablets and powders, in polymer powders and toners.

Experiment 4: HDK® as Thickening Agent, Adsorbent and Carrier

Weigh out 1.2-g-portions of HDK® N20 into different sealable glass vessels and add 5, 10, 15 and 20 g water. What happens in the vessels? How do the substances behave at rest or when agitated?

To several milliliters of silicone fluid in a test tube, slowly stir in 2 wt.% HDK® N20 and observe the change in viscosity. What happens to the air bubbles stirred into the mixture? Now liquefy the mixture again by slowly stirring in more silicone fluid.

Explanation:

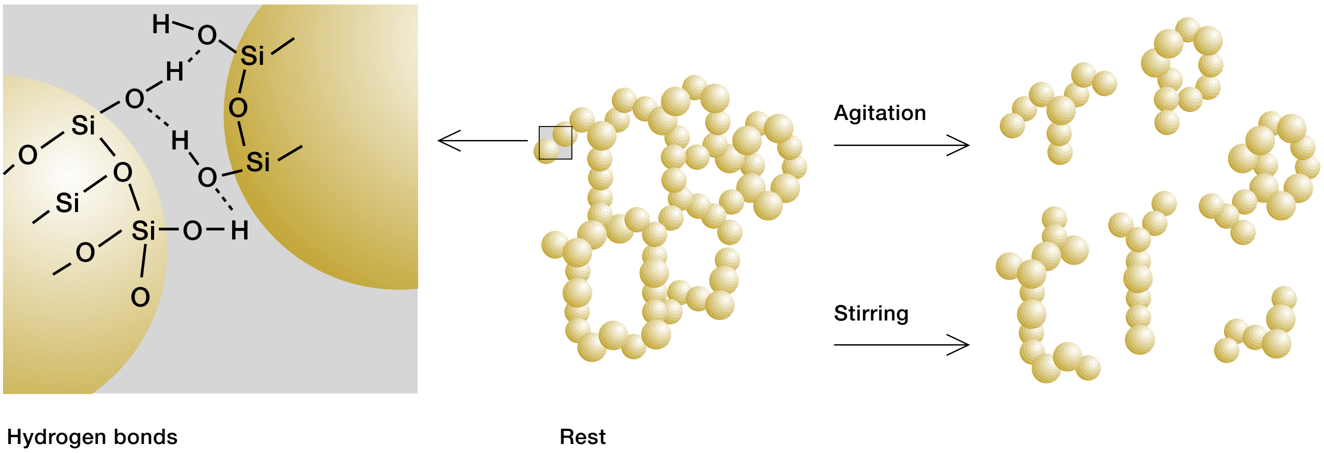
When fumed silica is dispersed in a liquid, the liquid becomes thicker due to the formation of hydrogen bonds between the primary particles. This generates a three-dimensional network of HDK® primary particles that restricts the mobility of the molecules in the liquid. The silica essentially solidifies the system. The liquid becomes stored in the interstitial particle volume of these agglomerates, and gaseous and liquid substances are adsorbed through the formation of hydrogen bonds. This network can be quickly destroyed by energy input or by mechanical stress, such as stirring or agitation (thixotropic effect). This ruptures some of the hydrogen bonds that were responsible for stability.

The molecules of liquid become more mobile, and the viscosity of the substance decreases. The stronger the force is and the longer it acts, the more linkage points are ruptured, and the more fluid the substance becomes. Since a certain amount of time is needed for the linkages to form again, the system remains liquid for some time (thixotropy).

Uses :

- As an additive for increasing the viscosity of gels, pastes, ointments and creams
- As an adsorbent and carrier for substances in essential oils, plant extracts and balsams
- Paints and adhesives must be easy to apply and flow and dry well, but they must not drip or run. HDK® is added to printing inks, adhesives, polymers and paints to make them easier to apply; when the viscosity is low, HDK® also forms a three-dimensional network that keeps fillers and pigments in suspension, and prevents them from settling out on the bottom.

Thixotropic effect of HDK®



Notes:

E3 SILICONE ANTIFOAM AGENTS

Chemical from the experimental kit:
SILFOAM® SRE

SILICONE ANTIFOAM AGENTS

E3.1 Digression: Surfactants – How is Foam Formed?

The drop of water on the water-repellent substrate (see Silicone Fluids) demonstrates the great importance of interfaces in many industrial and natural processes. The drop forms an interface with both the substrate and the air. The high surface tension of the water, which stems from the strong interactions between the water molecules, causes the droplet to take on a spherical shape.

The solid substrate therefore does not become wetted. But lowering of high surface tension – or interfacial tension in general – can be of vital importance in nature. For instance, we would be unable to digest the water-insoluble fats in our food if the aqueous system in our bodies could not absorb them. This task is performed by bile acids, which accumulate at the interface between water and fat and thereby lower the interfacial tension.

Substances that act as emulsifying agents in this way are therefore also known as surface-active compounds or surfactants.

Detergents and cleaning agents are the principal applications of surfactants, and account for 50 % of surfactant use. Surfactants, however, are also used as auxiliaries to produce special effects in textile and fiber production, and in shampoos, shower gels, skin oils and creams within the cosmetics industry. Further uses include enrichment of mining coal and ore, deinking of recycled scrap paper, and various applications in the foodstuffs, paint and surface coatings, and crop protection areas.

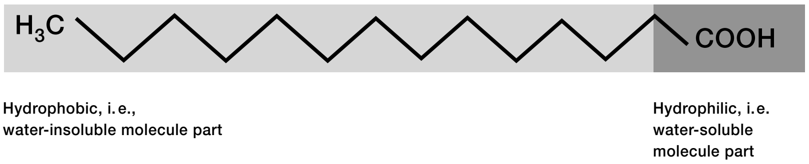
A typical formulation (recipe) for a modern compact detergent contains roughly 20 wt. % surfactants in addition to the builders (phosphate substituents) and the bleaching system.

Chemistry of surfactants

The essential properties of surfactants are the ability to foam, to wet skin, to emulsify dirt and grease, and the ease with which they can be rinsed off. These properties all stem from the typical structure of surfactants: each molecule has a part which is attracted to water (i. e., is hydrophilic) and a part which is attracted to oil (i. e., is hydrophobic). For instance, the taurocholic acid in bile is part hydrophobic hydrocarbon group from the steroidal backbone and part hydrophilic amidoalkylenesulfonate group.

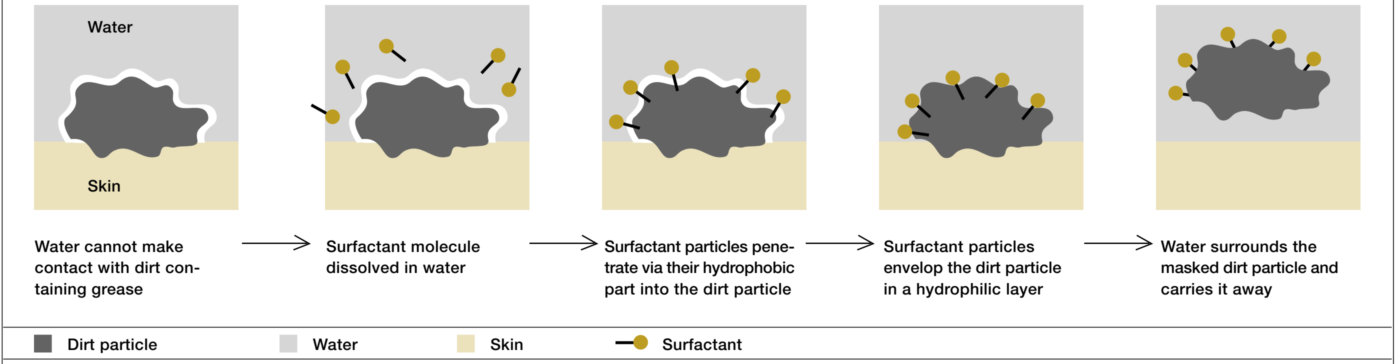
The oldest surfactants – soaps – have a similar structure, consisting of a hydrophobic, linear hydrocarbon chain and a hydrophilic carboxylate group:

Structure of a surfactant molecule (in this case: soap)



When such surfactant molecules are introduced into a two-phase system, they concentrate at the interfaces between the phases. By virtue of their concentration and orientation, they are able to modify the properties of the interfaces, i. e. they lower the surface tension. Consider, for instance, dirt particles adhering to fabric or skin. Lowering the surface tension causes them to become partially wetted and helps them to be dislodged.

Dislodging dirt with the help of surfactants



Because the charges of the soap anions are pointing outwards, the dirt particles are prevented from agglomerating together and thus remain suspended in the washing solution.

Foam is often defined along the following lines in the literature: **"A collection of gas-filled, spherical or polyhedral cells bounded by liquid, semi-liquid, high-viscosity or solid cell skins."** During foam formation, on the surface of liquid, i. e. at the liquid/air interface, each soap or surfactant anion aligns itself such that the hydrophobic alkyl group projects into the air and the hydrophilic end projects into the liquid. As the concentration of surfactant rises, the interfacial tension falls, and eventually the surface of the liquid is completely covered with surfactant molecules. The liquid's surface becomes progressively more like air; i. e. spherical bubbles of foam are formed. The liquid increasingly drains away from the bubbles, which consequently become thinner and thinner and huddle together, distorting each other's shapes and eventually becoming polyhedral (polyhedral foam).

This process is known as the drainage effect. However, the bubbles remain fairly stable if the surfactant can prevent the liquid from draining away completely. It can do this because, as the liquid drains away and the bubbles become thinner, the electrically charged hydrophilic groups of the surfactants draw closer and closer together and electrostatic repulsion increases. This prevents further drainage.

E3.2 WACKER Antifoam Agent SILFOAM® SRE – Mode of Action and Application

There are applications in which the cleansing power of surfactants is desired but their tendency to foam is not. In modern washing machines, for instance, foam suppression is essential to a clean wash. If over-foaming occurs, considerable amounts of wash-active substance may be lost. Furthermore, extensive foaming inhibits mechanical cleaning by the foam.

Washing processes are not the only application in which excessive foaming is frequently undesirable. Many industrial processes can be severely hampered by foam formation. Destroying foam can often shorten or simplify production sequences and lead to better products.

WACKER antifoam grades find application in a great many products and industrial processes:

1. In the textile industry during fiber manufacture and processing, in washing and dyeing processes
2. In the leather industry for dyeing and fat-liquoring leather
3. In the cleaning agents industry for controlled foam formation in general-purpose, glass, metal, disinfectant, sanitary and carpet cleaners, in floor polishes and paint removers
4. In detergents for regulating foaming
5. In the manufacture of paints and surface coatings to destroy foam during mixing, pumping and filling as well as during application (painting etc.) since foam can lead to surface defects
6. In the petrochemicals industry to defoam and degas crude oil during recovery, to assist in refinery distillation, as well as to defoam diesel fuel
7. In cooling lubricants, engine oils and metal-working fluids
8. In the agrichemical industry during the production and application of crop-protection agents and fertilizers
9. In the paper industry to enhance pulp manufacture, reduce its environmental impact and to reduce costs
10. In wastewater treatment to defoam effluents in sewage treatment plants as a means of supporting the purification process
11. In the pharmaceutical industry during the manufacture of liquid preparations, in fermentation processes and as an active ingredient for destroying gas bubbles in the human gut.

Since WACKER antifoam agents are used in a wide variety of applications throughout industry and therefore have to fulfill the most diverse requirements, they are produced in various forms, e. g. emulsions, liquids, powders and oils.

How antifoam agents work

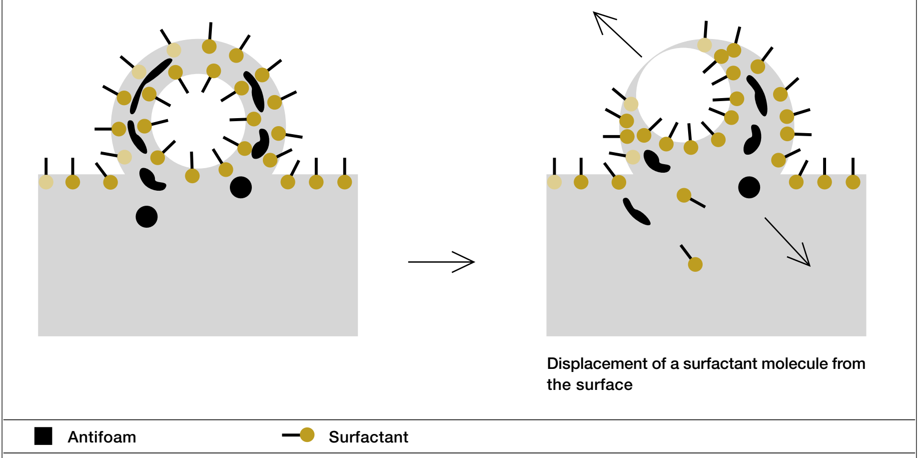
Antifoams are liquids or emulsions that have a low surface tension. They must fulfill three basic conditions:

- They must be insoluble in the medium to be defoamed
- They must have a positive penetration coefficient
- They must have a positive spreading coefficient

A positive penetration coefficient enables the antifoam to penetrate the foam lamella. If the antifoam also has a positive spreading coefficient, it will spread out at the interface once it has penetrated the lamella, i. e. it will displace the surfactant from the interface. The effect is to replace the elastic lamella by a film of lower surface tension and weaker cohesive forces. The action of such antifoam liquids in many systems can be greatly enhanced by adding finely dispersed hydrophobic solid particles. The antifoam liquid serves to transport the solid particles into the foam lamella. Inside the hydrophilic liquid lamella, the hydrophobic particles act as foreign bodies, destabilizing it by weakening the cohesive forces and adsorbing surfactant molecules onto their surfaces, thereby causing the foam lamella to collapse.

WACKER silicone antifoam agents contain silicone fluids that act as antifoam liquids. Silicone fluids are ideal for this purpose for a great many reasons. They are easy to chemically modify and lend themselves to a very wide range of applications, they are largely chemically inert, they do not adversely affect the wetting (cleansing) action of the surfactants and they are suitable for use in the pharmaceutical and food-

Destroying foam with a silicone antifoam agent



Displacement of a surfactant molecule from the surface related sectors. Because they have a low surface tension of approx. 21 mN/m, silicone defoamers have a strong tendency to spread over foam lamella. They can also transport hydrophobic particles (e. g. fumed silica) into the lamella. They may also contain penetration agents, e. g. emulsifiers, to help them penetrate the lamella.

E3.3 Combating Foam

Experimental Procedure

Experiment 1:

Take a vial with a snap-on lid and fill it two-thirds with water. Add several drops of dishwasher detergent. Close the lid and shake the vial vigorously. What do you observe? What happens to the foam as time passes? Describe what happens. Draw the various stages of foam formation (see spherical and polyhedral foam).

Experiment 2:

Using a pipet, take up several milliliters of the surfactant solution and wet different surfaces such as glass, porcelain, metal and paper with one drop each. Do the same with water. What happens? From your observations, what conclusions can you draw about the surface tensions of the water and the surfactant solution? Compare the angles formed with the contact angles discussed in **E1.2**.

Experiment 3:

Parallel to that, transfer identical surfactant solution into another vial, shake it vigorously (foam formation!) and add a drop of WACKER Antifoam Emulsion SILFOAM® SRE. What happens? What happens after you shake the vial again?

Experiment 4:

How well does the wetting ability of this solution compare with that of the pure surfactant solution and of pure water?

E4 SILICONES IN CONSTRUCTION CHEMISTRY

Chemical from the experimental kit:
SILRES® BS SMK 1311

SILICONES IN CONSTRUCTION CHEMISTRY

E4.1 WACKER Silicone Masonry Protection Agent SILRES® BS SMK 1311

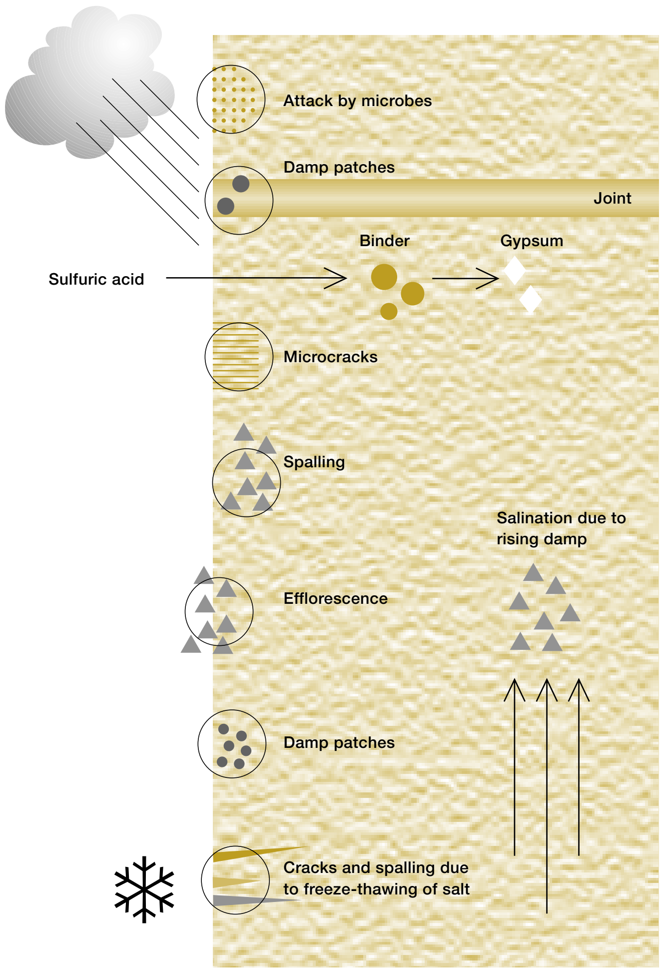
In principio erat aqua or, **water is the prime culprit.** Moisture is one of the most critical problems confronting planners, builders and house owners trying to protect buildings effectively. For, although there are many ways in which building materials can decay, absorption of water is always involved. Building materials are more or less porous in structure, being composed of channels, voids and caverns, which can become filled with water. When this happens, the material's thermal insulation properties break down. The absorbed water opens the door, as it were, to all kinds of serious damage.

The water can be absorbed in two forms:

a) **As liquid:** rainwater, vadose water, rising damp
b) **As vapor:** condensation in capillaries, hygroscopic moisture uptake, condensation

Whatever the mechanism involved, the masonry becomes saturated and susceptible to all kinds of weathering, as summarized below and shown in the diagram opposite:

Types of moisture damage on masonry and their causes



- Rainwater and water on the surface cause the binder to swell and contract and ultimately lead to mechanical damage and wash-out; joints are particularly prone to absorbing water, and damp enclaves are formed when they dry out.
- Microcracks caused by temperature fluctuations promote water uptake.
- Rising damp causes salt damage in the masonry; the salts are transported by the damp to the surface, or just below it, where they crystallize out.
- Deposition of salts just beneath the surface causes the building material to become friable; the bursting forces generated by crystallizing salts (which occupy more space) lead to spalling.
- Hygroscopic salts continually absorb moisture from the environment and cause the building material to become damp.
- Freezing and thawing of salts at ground level leads to cracking and spalling.

- Sulfuric acid in the atmosphere reacts with carbonates (in binders) to produce gypsum (“sulfate attack”) and carbon dioxide, which augment the bursting forces.
- Permanently damp facades suffer attack by moss and microbes (fungi and algae).

Damp masonry impairs thermal insulation. The way to prevent damage to buildings is therefore to stop water from penetrating into the masonry in the first place. There are two fundamentally different ways of accomplishing this, namely to apply either a coating that forms a continuous (essentially impenetrable) film or a water-repellent coating that does not clog the masonry pores:

- Film-forming surface treatments include resin solutions and coalescent paints. Although they seal off the masonry against water, they also clog the pores, with the result that the masonry loses its permeability to water vapor.
- Non-clogging water-repellents form hydrophobic molecular films that prevent water from penetrating into the building material, but do not lower the material’s water-vapor permeability. Silicones belong to this group.

Silicone masonry protection agents are used in the construction industry as:

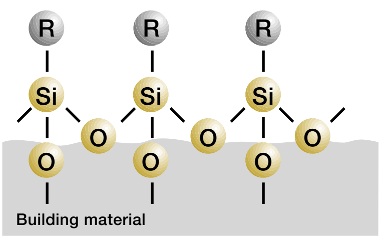
- **Water repellents** applied to standing buildings. The water repellent is colorless, does not form a continuous film and reduces moisture damage by preventing water and pollutants dissolved therein from being sucked in via the capillaries.
- **Stone strengtheners** for preserving national heritage objects made of natural stone. Stone cements that generate silicic acid gel inside the stone restore the original strength without altering the stone’s appearance.
- **Oil repellents** for protecting natural stone against organic contaminants such as oils, greases, waxes and adhesives.
- **Chemical damp-proofing agents** for making a horizontal barrier against capillary rising damp, particularly in old buildings.

The types of organosilicon compounds used vary according to application. They include siliconates (water-soluble salts of organosilicic acids), silane/siloxane mixtures (in organic solvents or as microemulsions) and silicic acid esters (for stone strengthening). These silicone compounds may be incorporated as a preventive measure into masonry paints, as binders or additives into building materials or they may be applied during the renovation and maintenance of standing buildings.

E4.2 How Silicone Masonry Water Repellents Work

Silicones are semi-organic materials. The inorganic backbone, which resembles quartz (SiO_2), has organic substituents (R). As a result, they have a special molecular structure. Each molecule aligns itself so that its inorganic part is nearest the building material, which has a similar structure, and its organic substituents project outwards. The organic substituents are hydrophobic and form a barrier against impinging water. The building material or fabric is now much less prone to become wetted because liquid water is unable to penetrate into the pores. Since the silicone water repellent does not seal the pores of the building material, water vapor is still able to pass back and forth. As a result, water vapor will not condense inside the building material and cause damage. However, water under high pressure can overcome the water repellency imparted by the silicones. Consequently, silicone water repellents used in masonry protection are unsuitable for sealing foundations. They are best suited to external facades, i. e. heavily inclined or vertical surfaces.

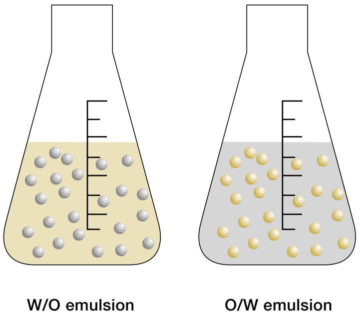
Molecular structure of silicones



E4.3 Digression: Emulsions – Microemulsions

Disperse systems of immiscible liquids are called emulsions. One of the two liquids forms an outer (continuous) phase containing the other (inner or discontinuous) phase in the form of fine droplets. The size of the dispersed droplets determines whether the system is called a macroemulsion or a microemulsion (colloidal dispersion). The droplets vary in diameter from 10^{-2} to 10^{-6} cm. Emulsions vary from clear to hazy, the degree of haze depending on the diameter of the dispersed droplets. The immiscible phases of most natural and industrial emulsions consist of water and either oil or grease/fat. If the outer phase is water and the inner phase is oil, the emulsion is said to be an oil-in-water emulsion (o/w emulsion); its properties are essentially those of the water (e. g. milk, mayonnaise, ice cream). Conversely, when water is dispersed in oil, we talk of an water-in-oil emulsion (w/o emulsion) (e. g. butter, margarine, ointments).

Immiscible fluids – emulsions



To make an emulsion, one liquid has to be dispersed in the other. This greatly increases the surface area of the dispersed liquid. Because of the interfacial tension between the liquids, the emulsion is unstable and could separate. An emulsifier is therefore added to lower the interfacial tension and enhance stability. Emulsifiers prevent emulsified droplets from agglomerating. They have the same structure as surfactants. In industry, emulsions are used as a means of transporting substances to places which they would never be able to reach in a pure form on account of interfacial tension or viscosity, e. g. through masonry pores and into capillary voids.

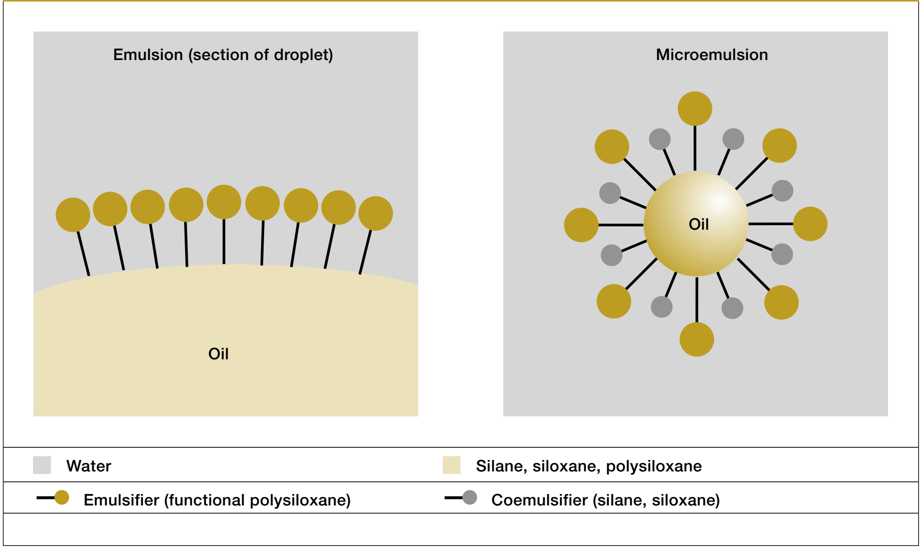
E4.4 Water-Repellent Treatment with SILRES® BS SMK

Silicone emulsions are unsuitable for impregnating building materials because their droplets are too big; the emulsions “break” on the surface of the materials, and form a dark, glossy film that does not penetrate to any great extent. For this reason, silicone emulsions are only used as water-repellent additives for gypsum, aerated concrete and paints.

WACKER has developed silicone microemulsion concentrates (SILRES BS SMK®) that are capable of impregnating building materials. SILRES BS SMK® grades are clear, low-viscosity liquids that do not contain any water or organic solvent. When diluted with water, they disperse spontaneously to form extremely fine, stable silicone microemulsions. These microemulsions are clear to translucent because their particle size, which ranges from 10 to 80 nm (10 - 80 x 10^{-7} cm), is less than one-fourth the wavelength of visible light. In technical parlance, they are classified as micellar solutions and referred to as monophase systems. Unlike classical macroemulsions, which consist of oil phase, water phase and emulsifier, microemulsions have four components, the fourth being a coemulsifier. Silicone microemulsions are o/w type emulsions, with an inner phase of silicone. The emulsifier is a surfactant that forms a “rigid” crystalline molecular layer around the droplets of the inner phase. These droplets therefore have little tendency to curve, and so their diameters will be greater than 1,000 nm (10^{-4} cm), i.e. a macroemulsion will be formed. The purpose of the coemulsifier is to soften the crystalline surfactant layer, and make it much easier to curve.

Using a coemulsifier results in the formation of tiny droplets with diameters ranging from 10 to 80 nm (10 - 80 x 10^{-7} cm) .

Comparison of a microemulsion with a normal emulsion



The difference in size between the particles of a macroemulsion and a microemulsion is similar to the difference in size between a house and a handball. Similarly, a microemulsion has a surface area 100 times that of a macroemulsion and so it needs a much higher concentration of emulsifier and coemulsifier to keep it stable. For this reason, silicones as coemulsifiers are used that can simultaneously serve as active agent and are capable of polymerizing out. The droplets themselves contain condensation-crosslinking components and belong to the class of silicone resins which yield a high crosslinking density.

The advantages of SILRES BS SMK® are:

- High effectiveness
- Ease of use
- Physiological compatibility
- Good compatibility with the environment since they do not contain any organic solvent
- High depth of penetration, even into damp masonry

E4.5 Microemulsion and Water Repellency. Experimental Procedure

Experiment 1: Preparing a Microemulsion

Stir several drops of SILRES® BS SMK 1311 concentrate into a glass beaker containing water. A whitish but translucent solution forms. Hold a flashlight or, better, a laser pointer against the beaker and follow the light beam in the emulsion (Tyndall effect, nephelometry) and then contrast it with a clear solution (e. g., sugar or common salt in water).

What causes this effect? What is meant by scattered light and why does this effect not occur in one of the solutions?

Experiment 2: Water-Repellent Treatment of the Aerated Concrete Brick Provided

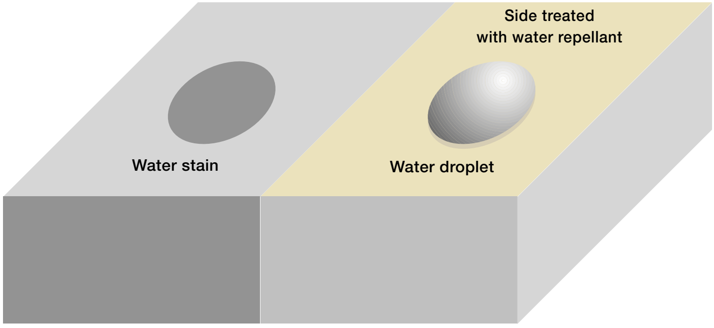
Fill a glass beaker with 100 - 200 ml of water. Stir in an amount of SILRES® BS SMK 1311 microemulsion concentrate equivalent to 1/10th of the mass of water. A yellowish-white emulsion forms.

Immerse half of the aerated gas brick into the emulsion and take it out again after 5 minutes. You could also use the emulsion to impregnate other building materials, e. g., a small flowerpot or piece of concrete. Allow the immersed building material to dry in air. After just one day, the treated section of the aerated gas brick exhibits a marked water-beading effect whereas the untreated section absorbs drops of water immediately.

The effect is particularly striking with this type of building material because the large pores give the impression that the water droplets are floating on the brick. With other building materials, the water-repellent effect may take three days to develop.

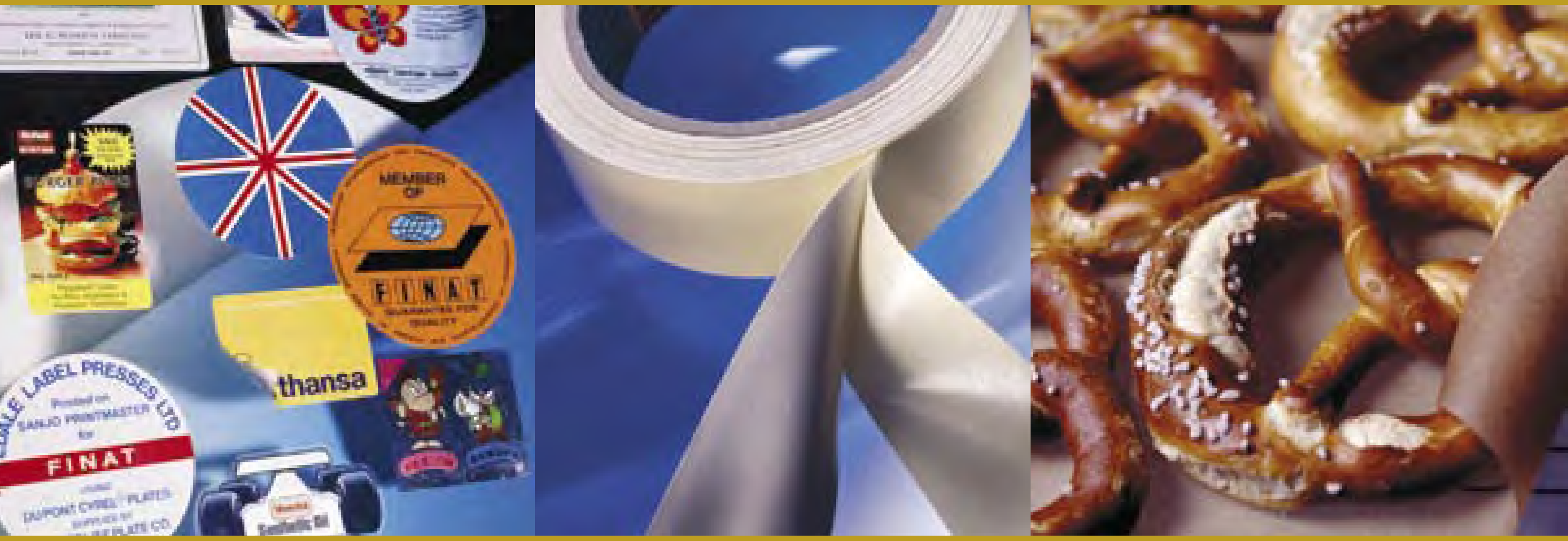
The aerated gas brick can be kept for years for demonstration purposes. The emulsion solution is stable only for about 24 hours, after which it starts to become ineffective.

Aerated gas brick, half treated with SILRES® BS SMK 1311



Notes:

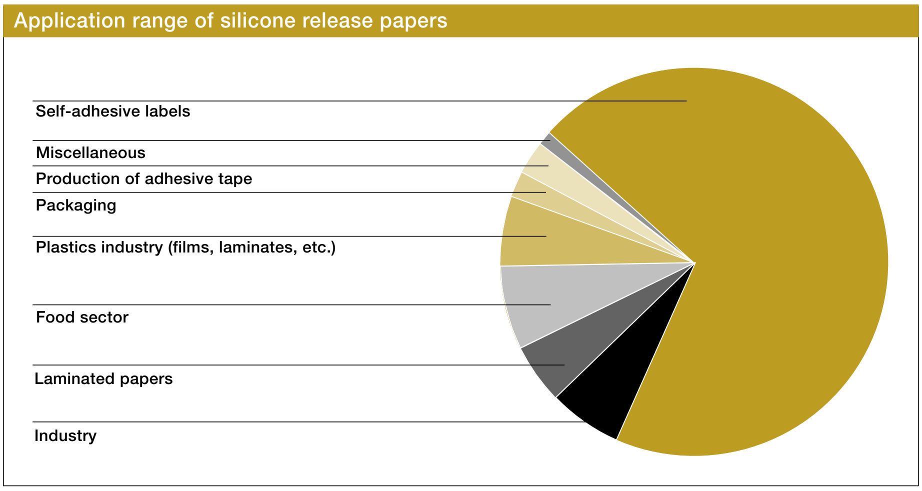
E5 DEHESIVE® SILICONE RELEASE PAPERS – SO LABELS STICK WHERE THEY SHOULD



Chemicals from the experimental kit:
DEHESIVE® 920
WACKER® CROSSLINKER V 24
WACKER® CATALYST C 05

DEHESIVE® SILICONE RELEASE PAPERS – SO LABELS STICK WHERE THEY SHOULD

Application range of silicone release papers



E5.1 Applications and Chemical Principles

Paper and film or foil can be coated with crosslinkable silicones to produce silicone release papers that are used in a wide range of applications.

For reasons of price and quality, the silicone is applied as an ultra-thin, uniform coat. It is chosen for its ease of processing before application and its speed of crosslinking afterwards. What is the basic structure of a self-adhesive label?

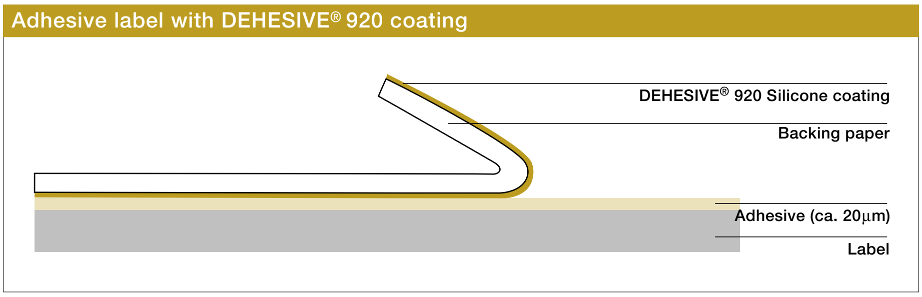
The backing paper to be coated is usually very dense, e. g. glassine, clay-coated or so-called Kraft paper; this has very low absorbency and low penetration, which means that the silicone coating forms a smooth surface when it is applied. Various plastic films (PE, PP, PVC) can also be coated with silicone. Special coating machines are needed for coating all these materials.

DEHESIVE® grades are supplied in the form of three components as this provides maximum flexibility in preparing tailor-made coatings.

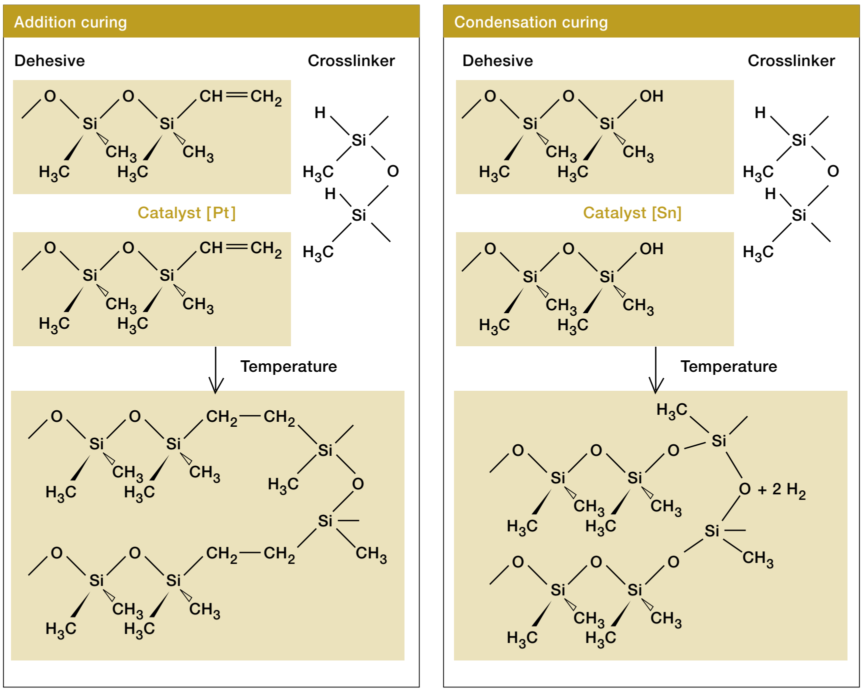
The components are:
- **Polymer** (DEHESIVE®):
  Solvent-free, addition or condensation-curing polymethylsiloxanes
- **Crosslinker:** Polyhydrogensiloxanes with a high content of reactive Si-H for thermal addition-curing systems; the nature and quantity of crosslinker influences the rub-off resistance and adhesive properties of the silicone film.
- **Catalyst:** Mainly highly reactive platinum complexes (0.1 %, 1,000 ppm) for thermally curing silicones; the quantity of catalyst employed determines the production speed, crosslinking temperature and the pot life (i. e. the maximum period over which the prepared mixture can still be used).

If the release force has to be increased, a so-called Controlled Release Agent CRA® (not included in the experimental kit) may be added. This contains special silicone resins that make the adhesive on the label adhere more strongly to the silicone coating. The extent of the increase is determined by the nature and quantity of the CRA® additive used. There are controlled release additives available for matching silicone release papers to all types of adhesive used.

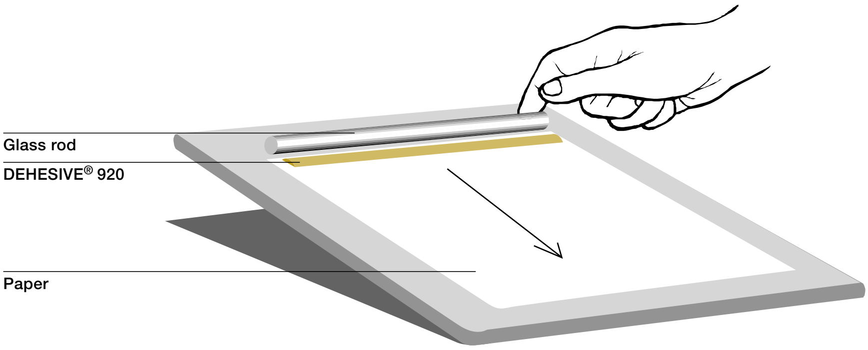
Adhesive label with DEHESIVE® 920 coating



Chemical reactions



Coating paper with DEHESIVE® 920



E5.2 Coating Paper with DEHESIVE® 920

Experimental Procedure

These instructions for preparing the reactive solution for coating paper with silicone must be carried out strictly in the order given:

Add 1.3 g WACKER CROSSLINKER V 24 to 50 g DEHESIVE® 920 and stir vigorously with a glass rod. Then add 0.5 g of WACKER CATALYST C 05 and again stir vigorously. The resultant liquid is used for coating and has a shelf life of about 24 hours. It can now be applied to different types of paper.

Perform the coating as follows:

1. Clamp or tape the paper to a flat, solid, washable surface.
2. Apply a bead of coating agent to the top end from a pipet.
3. Use a thick glass or metal rod to spread the mixture over the paper by pressing the rod firmly onto the paper and drawing it downwards.
4. Then place the paper for 30 to 60 seconds in a drying cupboard or oven at 100 to 150 °C. These conditions are sufficient to fully cure the coating.

The oven temperature may be varied (e. g. room temperature, 50 °C, 100 °C) to show how it affects the crosslinking speed.

If highly absorbent paper is used (e. g. normal photocopying paper), the whole process can be repeated. The release action can be tested very simply using Scotch tape: the tape detaches easily from coated paper but clings to untreated paper. In conjunction with the experiments on making adhesives (**E10**), you can now produce your own sticker.

E6 ELASTOSIL® M – THE CHARM OF REPRODUCTIONS

Chemicals from the experimental kit:
ELASTOSIL® M 4601 A
ELASTOSIL® M 4601 B
ELASTOSIL® M 4400
WACKER® CATALYST T 37

ELASTOSIL® M –
THE CHARM OF REPRODUCTIONS

E6.1 Cold-Curing, 2-Component Rubbers

The key components of silicone rubber are silicone polymers and fillers. Chemically modified linear silicone fluids can be made to crosslink to form more or less wide-meshed structures having pronounced elastic behavior. Adding fillers (e. g. HDK®, calcium silicate, calcium carbonate) to the mix will yield a silicone rubber with characteristic properties.

Crosslinking can be effected at ambient or at higher temperatures by the usual methods employed in the rubber industry. The crosslinking mechanism determines the density of crosslinks in the cured rubber and thus has a crucial influence on its properties. The RTV silicone rubbers (room-temperature vulcanizing) contained in the experimental kit crosslink by condensation and addition reactions. Whereas only atmospheric moisture is needed for crosslinking RTV-1 silicone rubber (cf. experiment **E7**), a second component is required for RTV-2 rubbers.

Condensation crosslinking is based on the reaction between α,ω-dihydroxypolydimethylsiloxane and silicic acid esters in the presence of catalysts such as dibutyltin laurate and tin (II) octoate. The reaction rate depends on the functional groups contained in the crosslinker, its concentration, its chemical structure and the type of catalyst.

Addition crosslinking entails addition of Si-H across double bonds. The catalysts employed are salts and complexes of platinum (or palladium or rhodium). Olefin complexes of platinum metals are used for crosslinking at room temperature. Nitrogenous platinum complexes (platinum complexes of pyridine, benzonitrile, benzotriazole) are used at elevated temperatures.

Properties of silicone rubber

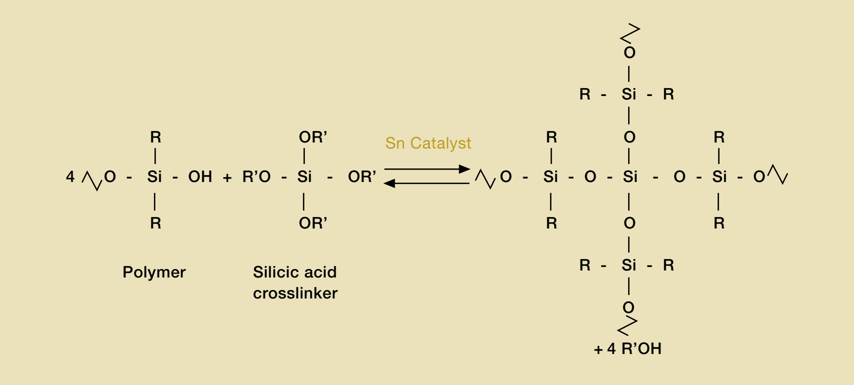
Silicone rubbers have unique properties. Foremost among these are:

- Flexibility largely unaffected by changes in temperature
- Great resistance to heat and cold
- Mechanical properties only slightly affected by changes in temperature
- Flame resistance
- Electrical insulation
- High chemical and oil resistance
- Non-stick properties, i. e. high release action
- Gas permeability
- Good damping properties for shock and noise
- Compounding versatility, i.e. organic substituents can be varied.

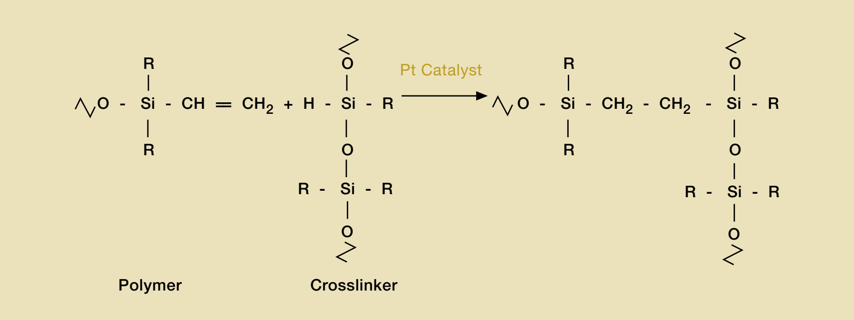
The crosslinking of silicone rubber

Condensation crosslinking	Addition crosslinking
Blending ratio of silicone rubber and catalyst variable within limits	Blending ratio of both rubber components is fixed
Crosslinker and catalyst both contained in catalyst	Crosslinker present in rubber component A; catalyst (platinum complex) in rubber component B
Curing impaired only by lack of water	Curing impaired by different substances (sulfur compounds etc.)
Curing rate largely independent of temperature	Curing rate heavily dependent on temperature
Chemical shrinkage due to cleavage of alcohol	Practically no shrinkage
Cleavage products (alcohol) may cause depolymerization already from 80 °C	No reversion
Long pot life and hence long curing times	Long pot life but curing can be accelerated by exposure to high temperatures

Condensation curing of RTV-2 silicone rubber



Addition curing of RTV-2 silicone rubber



E6.2 Molding an Object with RTV-2 Rubber (Addition Curing)

Experimental Procedure

The two-component silicone rubber ELASTOSIL® M 4601 is a pourable rubber that cures quickly at room temperature without shrinking. Its special mechanical properties make it ideal for all kinds of molding applications. The crosslinker is contained in component A and the platinum catalyst is contained in component B.

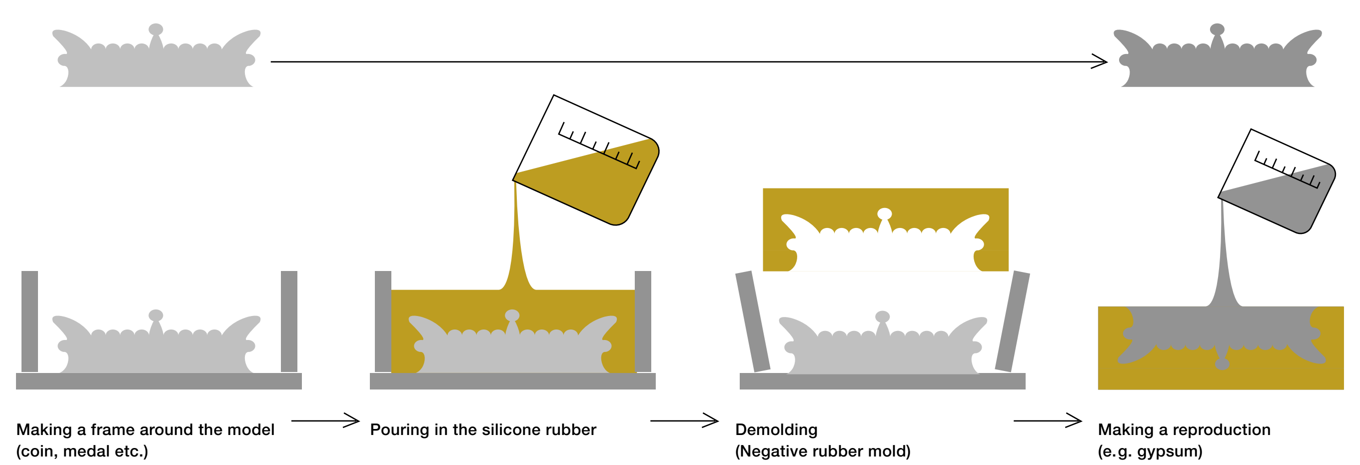
Processing

Equipment:

Balance, clean metal or plastic containers, spatula, glass rod, perhaps desiccator

1. **Preparing the components:** Thoroughly stir up all pourable compounds before use to ensure that the fillers are uniformly dispersed.
2. **Metering and mixing the components:** Weigh out the components exactly as only strict observance of the mixing ratio ensures reproducible pot life and curing times. Mix the components of ELASTOSIL® M 4601 A and B in the ratio 9:1 (parts by weight). Weigh separately and then mix them until they turn a uniform wine-red. ELASTOSIL® M 4601 has a pot life of 3 hours at 15 °C and of 40 minutes at 30 °C.
3. **Removing the entrained air:** Air may be removed from the catalyzed mix by applying a vacuum in a desiccator. **Caution!** The mix expands extensively during evacuation, so do not fill the vessel to more than one-fourth of its total volume. During evacuation, the compound rises and then usually collapses.

Mold-making with ELASTOSIL® M yields exact copies



If the compound is likely to overflow, admit some air and repeat the process.
It is often unnecessary to remove air and this step can also be omitted if time is short.

4. **Applying the mix to the model:**
   Place the object to be molded on the base of the mold (alternatively, use a flat-bottom yogurt tub) and carefully pour in the mixture.
5. **Demolding the object:**
   When curing is complete and the mix has solidified, the model may be demolded. Note that the curing time depends heavily on the temperature. For example, the curing time is 12 hours at 23 °C, 20 minutes at 70 °C and 5 minutes at 150 °C. The temperature dependency of this addition crosslinking reaction can be demonstrated by allowing two batches to fully cure, one at room temperature and the other at 100 °C in an oven.
6. **Making the reproduction:**
   Molds made of addition-curing ELASTOSIL® M grades may be used for making reproductions as soon as they have been removed from the model.

Reproductions can be made in the following materials:
- Waxes
- Gypsum; treat new, unused molds with soap to prevent the gypsum from bubbling
- Casting resins, such as polyester, polyurethanes and epoxies; these materials cause extensive wear to the molds
- Metal alloys, but only those with melting points up to 300 °C
- Foods (e. g. chocolate, marzipan, ice-cream)

Where molds consist of two parts, a release agent (e. g. silicone fluid) must be applied to the two rubber parts to prevent their sticking together.

Catalyst poisons

A large number of substances prevent the platinum-complex catalyst from performing properly. These so-called catalyst poisons or inhibitors can inhibit or delay curing when they come in contact with the uncured catalyzed mix. Curing can be inhibited or delayed by adding sulfur, substances containing amines, or T-Series WACKER® CATALYST T 37.

E6.3 Molding with RTV-2 Rubber (Condensation Curing).

Experimental Procedure

The RTV-2 silicone rubber ELASTOSIL® M 4400 is a pourable, two-component silicone rubber that undergoes condensation curing at room temperature. It has good flow and self-deaerating properties, low hardness and great extensibility and flexibility.

ELASTOSIL® M 4400 is activated by adding T-Series WACKER® CATALYST T 37. This catalyst contains a tetraorganic tin compound. It is flammable and can irritate the eyes and skin. Therefore, take appropriate safety precautions (see also Material Safety Data Sheet)! The pot life and vulcanization time of the silicone rubber vary with the quantity of catalyst added. In order to be able to cure, especially when applied in thick layers, condensation-curing silicone rubbers require the presence of small quantities of moisture in the activated mix; normally, this moisture is already present. The curing time is largely independent of the temperature. Curing liberates alcohol, usually methanol or ethanol. Evaporation of the alcohol leads to a loss of mass, causing the cured rubber to shrink (by less than 5 %).

Processing

Transfer the ELASTOSIL® M 4400 to a glass beaker and weigh. Stir in 2 - 3 wt % T-Series WACKER® CATALYST T 37 using, e. g. a glass rod, taking care not to entrain any air. Now use the yellow mixture to make a mold of the object as described in the previous experiment. This mixture has a pot life of 90 minutes and needs 9 to 12 hours to cure. Demold after 24 hours to obtain a perfect bubble-free mold that is ideal for making reproductions.

If the amount of catalyst added is less than that stipulated, the rubber will not cure properly and will remain soft or tacky. If too much is added, the rubber may be much weaker than it should be. A curing temperature between 0 °C and 70 °C max. is suitable. Temperatures exceeding 80 °C will cause the reaction to go into reverse (depolymerization occurs). Signs of this reversion are that the system becomes tacky and liquid again.

Suggestions for other experiments

The condensation reaction – the formation of a volatile, low-molecular compound – can be demonstrated by weighing before and after curing.

Another experiment would be to stand a batch at >80 °C in a drying cabinet, which will prevent curing. In parallel, prepare a batch at 40 °C and another at room temperature to demonstrate that the reaction is not dependent on the temperature.

E7 ELASTOSIL® SILICONE SEALANTS – FOR AQUARIUMS

Chemical from the experimental kit:
ELASTOSIL® E 43 transparent

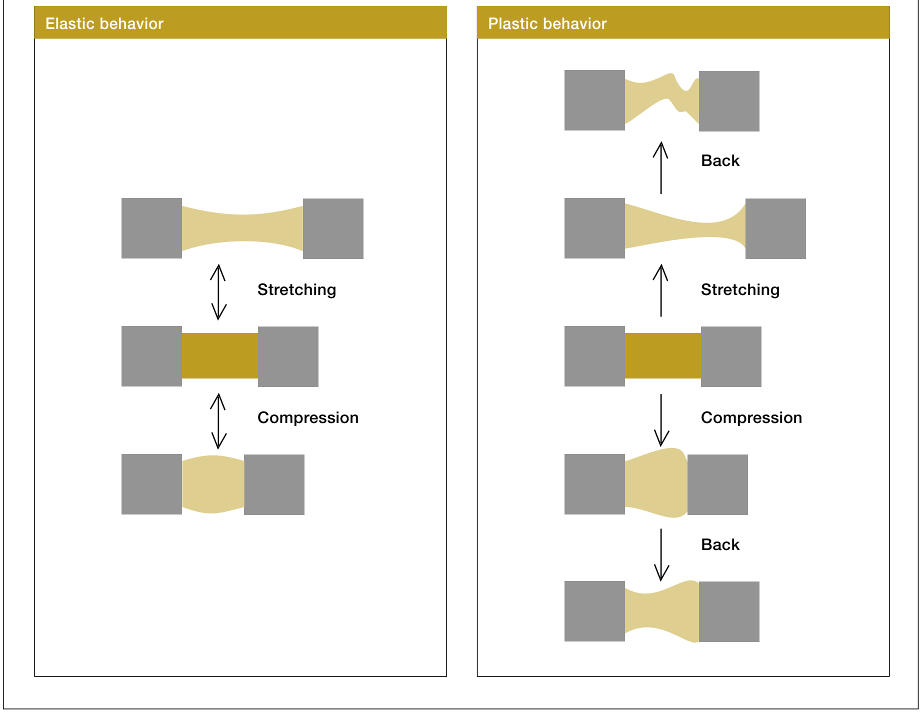
ELASTOSIL® SILICONE SEALANTS – FOR AQUARIUMS

E7.1 Joint Sealants – Applications

Silicone joint sealants are used in a wide variety of applications. RTV-1 silicone rubbers, consisting of one component vulcanizing at room temperature, are particularly popular because they are easy to use and have excellent properties. These 1-component compounds are somewhere between pourable and pasty and they react with atmospheric moisture to form a flexible silicone rubber. They are the answer to many sealing, bonding and coating problems in the automotive, shipbuilding and aviation sectors, in the electrical and electronics industries, and mechanical engineering. Their chief use is in the construction sector, where they are used for all kinds of projects involving glazing, jointing of natural stone, plastics engineering, civil engineering, sanitary applications and structural glazing (frameless glass panes bonded to facades).

Buildings constantly experience movements and stresses that may originate in thermal fluctuations, moisture phenomena, shrinkage of building materials, mechanical fluctuations, settling of foundations, etc. All these movements cause the masonry to crack. The only way to prevent such cracking is to install flexible joints. Sealants need to be particularly flexible wherever different materials (glass/metal, stone/metal etc.) are joined together because the materials will expand and contract by different amounts (they have different coefficients of expansion). Movement of 3 to 5 % can be accommodated by plastic compounds, but for elastic compounds this figure is 15 to 25 %.

Plastic and elastic behavior of polymers



Not only are silicone sealants flexible, but they also have extremely long service lives because they are highly resistant to weathering, radiation and chemicals. They adhere well to most substrates and their extensibility is constant over a wide temperature range (-30 °C to +80 °C). All the grades remain elastic up to 150 °C, and specialty grades up to 250 °C.

In many applications, it is crucial for the joint sealant to resist sagging immediately after it has been squeezed from the tube. This non-sag property (thixotropy) is conferred by HDK® as the major filler in silicone joint sealants.

E7.2 Chemical Composition of an RTV-1 Silicone Rubber

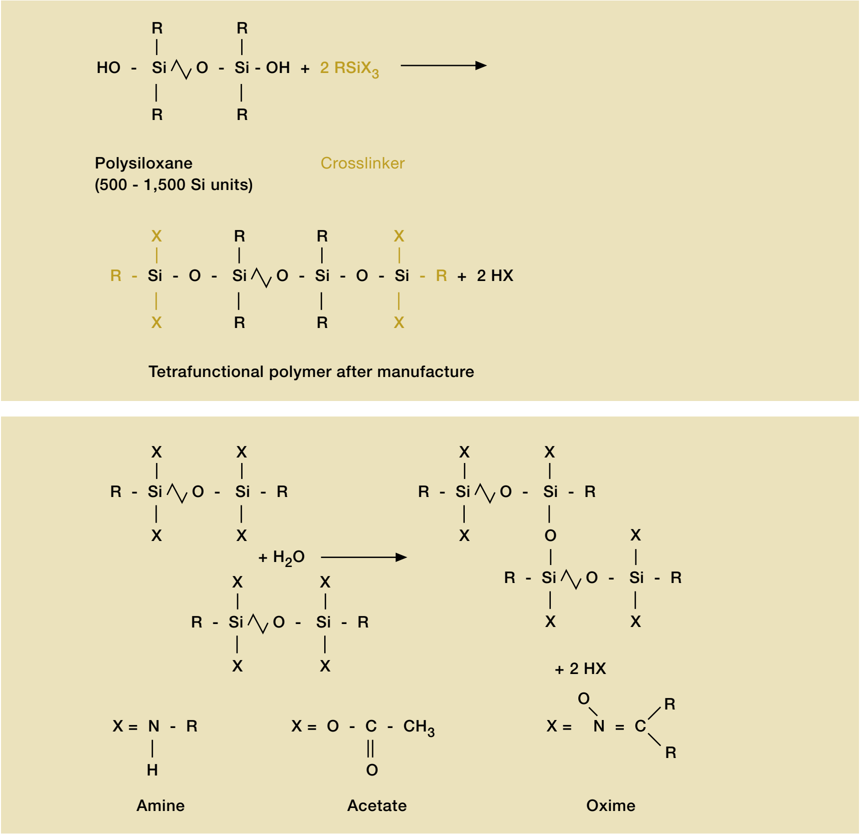
WACKER RTV-1 silicone rubbers consists of polydimethylsiloxanes, crosslinkers, fillers, and, in some cases, solvents and auxiliaries. During manufacture, terminal hydroxy groups on the polysiloxane react with the crosslinkers to form cur-able products. Curing is triggered by exposure to atmospheric moisture and is accompanied by the release of byproducts. Also known as vulcanization, this reaction starts with the formation of a skin on the surface of the silicone rubber and gradually works its way in. The sealants are packaged in sealed containers (tubes, cartridges) to prevent premature curing. The mechanism by which the sealant system cures depends on the crosslinker employed:

a) **Basic systems:** Release small quantities of an amine during curing (“A” types)

b) **Acetoxy systems:** Release small quantities of acetic acid during curing (“E” types)

c) **Neutral systems:** Release small quantities of an oxime during curing (“N” types)

The curing mechanisms of RTV-1 silicone rubbers



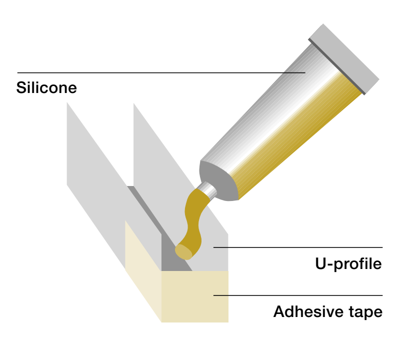
E7.3 Properties of Sealants Experimental Procedures

Experiment 1:

Builders are always faced with the difficult question of choosing the right sealant. Seals and joints in the home are often made with gypsum and silicone. Let us try a simple experiment to demonstrate the properties of silicones and gypsum to decide the suitability of each for various types of joints.

Cover the ends of three U-shaped profiles with adhesive tape, as shown. Fill one with ELASTOSIL® E 43 Silicone Sealant, ensuring that there are no gaps, and press the compound down with a wet finger. Fill the second profile with gypsum, again ensuring there are no gaps, and scrape off the excess with a spatula. If no profiles are available, use empty matchboxes. Place a thermometer in each sealant, allow the sealant to harden (several hours) and then paint over with watercolor.

Filling a U-profile with sealant



Observation tasks

Examine the three sealants and draw up a table of the following properties:

1. Odor
2. Change in temperature during curing
3. Impact strength
4. Consistency
5. Ease of painting with watercolor

Do chemical reactions occur during curing? Which sealants should be used for which application on account of their properties? Why are the acetoxy compounds used mainly for glass and glazed surfaces but not for marble, limesand brick and some metals?

Experiment 2: Influence of Atmospheric Moisture

Fill another U-profile with silicone sealant and, in parallel to the experiment above, store in a desiccator over dry silica gel under a water-jet vacuum.

What do you notice about curing in this case? What is the material’s consistency after one day and one week?

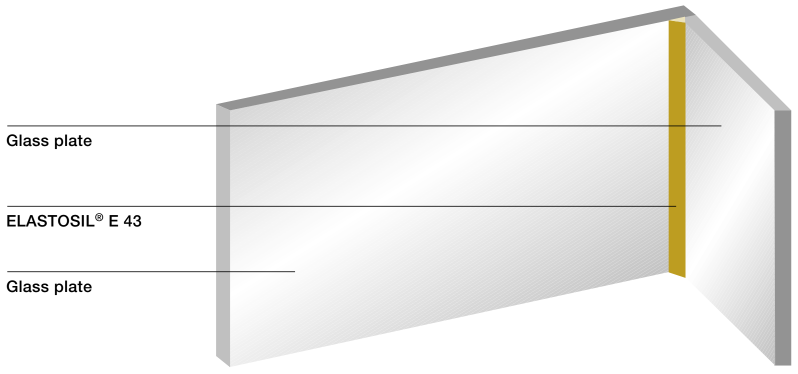
Experiment 3:
Building an Aquarium

Build an aquarium by using RTV-1 rubber sealant to join grease-free glass plates (clean with acetone or ethanol) to produce watertight seals. Join the glass plates together at right angles using ELASTOSIL® E 43 and leave over night.

A skin forms on the polymer within 25 to 40 minutes and an elastic compound forms after several days. Why does skin formation occur very quickly but final curing take quite some time?

By bonding 5 glass plates to each other (4 side walls and a base), you can make a small, watertight aquarium that can be used in the earlier experiment for impregnating a brick. Alternatively, you can use tiles instead of glass plates.

Bonding glass plates with an RTV-1 rubber



E8 HTV SILICONE RUBBER – FLEXIBLE AND IDEAL FOR MOLDING

Chemical from the experimental kit:
RTV Slabs

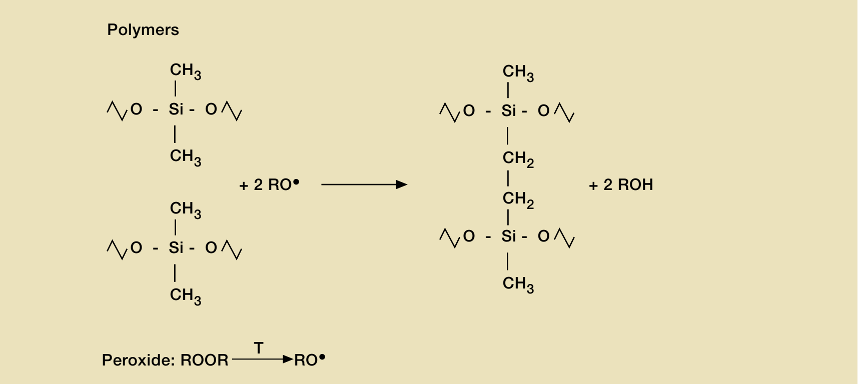
HTV SILICONE RUBBER – FLEXIBLE AND IDEAL FOR MOLDING

E8.1 Free-Radical Polymerization and Properties of ELASTOSIL® R

Silicone rubbers are classified into different categories mainly in accordance with the underlying base polymer and the crosslinking mechanism. In addition to the room-temperature-vulcanizing silicone rubbers (RTV) (cf. **E6**), there are rubbers that need high temperatures to vulcanize (HTV). Known at WACKER as ELASTOSIL® R, they have a wide range of outstanding properties that make them ideal for many applications, including those involving extreme conditions. HTV silicone rubbers are blends of high-molecular polydiorganosiloxanes that vulcanize at high temperatures. The base polymer is very viscous and has chain lengths of 10,000 silicon units and molecular weights ranging from 400,000 to 1 million. The rigidity of the Si-O polymer backbone can be modified and its properties varied by incorporating alkyl, alkenyl, vinyl, phenyl or trifluoropropyl groups. These linear polymer chains are the basis of the silicone rubbers.

HTV silicone rubbers are vulcanized at elevated temperatures, usually in the presence of an organic peroxide (free-radical crosslinking).

Mechanism of free-radical vulcanization in HTV silicone rubbers



Organic peroxides of the general formula R-O-O-R decompose at elevated temperatures into highly reactive free-radicals that join the linear chains of the polymer matrix together. The decomposition can also be initiated by high-energy radiation, such as UV light and microwaves. The result of vulcanization is a three-dimensional network in which the plastic rubber has been converted into an elastomer.

Peroxide-initiated vulcanization occurs faster if vinyl groups are present – they have a lower activation energy than methyl groups. Varying the density of the vinyl groups in the base polymer affords a means of controlling the crosslinking density. Replacing some of the methyl groups by phenyl groups yields silicone rubbers that remain flexible down to -90 °C.

Elastomers produced from HTV rubbers have a wide range of outstanding properties:

- Suitable for applications in the range -50 °C to +200 °C; specialty grades can be used from -90 °C to +300 °C
- High aging resistance, even when exposed to severe stress, e.g. ozone, hot steam
- Good resistance to many chemicals
- Outstanding electrical properties
- Good physiological tolerance
- Simple economic processing on standard machines used in the plastics industry, such as presses, injection molding machines, extruders, calenders
- A large range of color designs possible

HTV silicone rubbers – used in a wide range of applications

Automotive	Electrical	Foodstuffs, drugs	Construction	Machinery
Seals for: drive shafts, valves, oil pans, headlamps, sliding roofs, radiators etc.	**Cables for:** industrial plants, electric ovens, microwaves, cookers, grills, irons, heaters, coffee percolators, x-ray apparatus, halogen lamps etc.	**Seals for:** coffee machines, beverage dispensers, thermoses, steam cookers, microwave ovens, sterilization cupboards, etc.	**Profiles for:** jointing tapes, dry glazing, facade seals, window frames, structural glazing	**Rollers for:** photocopiers, plastics, textiles, papers, ceramics, wood, glass processing
Protective caps for: spark plugs, distributors, headlamps, spark plugs etc.	**Keyboards for:** calculators, computer games, telephones, remote controls, switch covers, insulators, cable sleeves etc.	Dialysis tubes, anesthetic masks and tubes, resuscitator bags, bungs, seals, valves and membranes for medical devices	**Emergency cables for:** power stations, high-rise buildings, subway trains	O-rings, valves, conveyor belts, flat seals, bellow expansion joints etc.
Hose for: cooling systems, heating systems, turbo chargers, ignition cables, door stops etc.				

WACKER is the world leader in the technology of hot-vulcanizing silicone rubbers. Due to their outstanding combination of product and processing properties, HTV silicone rubbers have high technology and market potential, and are used in a wide range of applications.

A specialty application is industrial safety cables. When used in critical areas of public buildings, HTV silicone rubbers ensure that cables keep functioning for a protracted length of time in the event of fire. Consequently, vital control and communications systems can be kept operational even at fire temperatures exceeding 900 °C. Whereas normal silicone rubber burns to a powdery ash, a new, specialty blend forms an electrically insulating shell around the live wire and keeps it functioning.

E8.2 ELASTOSIL® R – The Material with a Wide Range of Properties

Experimental Procedures

The special properties of the three colored slabs of HTV rubber supplied (white, blue and black) will be compared with those of conventional polymers (e. g. from a demonstration polymer set):
White: Low-temperature resistant
Blue: Flame resistant
Black: Heat resistant

Hot air
The goal is to compare the effect of heat on the various silicone rubbers and the reference polymers. Test whether the polymers soften or not on careful heating (thermoplastics or thermosets). Use a normal oven or a drying cabinet for this.

The properties of silicone rubber are affected much less by heat than are those of other elastomers (see black slab). In this regard, attention should be drawn to the excellent ozone and radiation resistance of silicone rubber that manifests itself in outstanding weathering resistance.

The resistance of silicone rubber to elevated temperatures may be described as follows:

At 150 °C:	2-4 years
At 200 °C:	1 year
At 250 °C:	100 days
At 300 °C:	Approx. 14 days

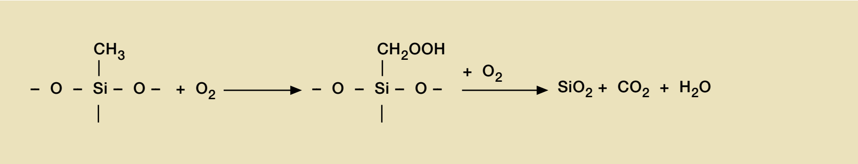
Temperatures up to 180 °C cause only very gradual changes in the properties of silicone rubber. Certain additives (carbon black, iron oxide etc.) may be incorporated to confer pronounced high-temperature resistance of up to 250 °C. Temperatures up to 900 °C will be withstood, provided that exposure is very brief. Up to 200 °C, mechanical properties deteriorate but this is reversible; after exposure to 200 °C, the rubber will regain its original tensile strength, provided that the silicone polymer has not undergone any thermal degradation. At temperatures above 200 °C, the organic substituents attached to the silicon undergo free-radical cleavage, with the result that additional crosslinking sites are created between the polymer chains. This irreversible chemical process manifests itself as a loss of weight. It is accompanied by shrinking of the rubber parts and increasing embrittlement. As a result, there is an increase in hardness, drop in tensile strength and impairment of tear strength. Nevertheless, the insulating power remains virtually the same and the rubber starts to acquire the insulating properties of quartz.

Under extreme heat, the fillers lead to hydrolysis of the polymer chains, and the rubber softens. If the temperature is high but no oxygen is present, the rubber starts to depolymerize and becomes useless. The rubber is therefore only very resistant to heat if atmospheric oxygen is present. Silicone rubber can withstand exposure to steam at temperatures up to approx. 130 °C for long periods. Consequently medical equipment made of silicone rubber may be safely sterilized in steam.

Combustion
The goal is to study how various polymers behave in the flame of a burner. Observe the flammability of the polymers and the odor of the combustion gases (fan the gases carefully towards the nose!). If the polymers soften before they decompose, describe the flame with which they burn and the combustion residue.

The auto-ignition temperature of cured ELASTOSIL® R rubber is about 430 °C. The flame burns at a temperature of 750 °C. Silicone rubber burns to form a white ash consisting of silicon dioxide that nonetheless has excellent dielectric properties. Very little smoke is evolved on burning. More importantly, combustion does not produce toxic or corrosive gases such as hydrogen chloride or sulfurous compounds.

The reactions involved in burning silicone rubber



$$-O-\overset{\overset{CH_3}{|}}{\underset{|}{Si}}-O- + O_2 \longrightarrow -O-\overset{\overset{CH_2OOH}{|}}{\underset{|}{Si}}-O- \xrightarrow{+\ O_2} SiO_2 + CO_2 + H_2O$$

Special additives can be incorporated into silicone rubber (e. g. TiO_2, platinum or aluminum compounds) to produce compounds that are highly flame resistant, and that may even be rendered self-extinguishing (see blue slab).

Low-temperature resistance
The goal is to study the flexibility of various polymers at low temperatures. Place the various slabs in a freezer and then test their flexibility.

Silicone rubber has excellent flexibility at extremely low temperatures. Specialty low-temperature grades can withstand temperatures ranging from -60 °C to -120 °C. The crystallization and glass transition temperatures drop abruptly when phenyl groups have been incorporated (see white slab).

E9 “BOUNCING PUTTY” – PLASTICITY AND ELASTICITY IN ONE

Chemical from the experimental kit:
WACKER® BOUNCING PUTTY 29

“BOUNCING PUTTY” – PLASTICITY AND ELASTICITY IN ONE

E9.1 Viscoelasticity

Polymers also differ from other materials in having special mechanical properties. When subjected to continuous pressure (e. g. when loaded down by their own weight), they begin to flow like a high-viscosity fluid, but when exposed to a brief, rapid force, they behave like elastic bodies. This property is known as viscoelasticity.

It is caused by secondary valence forces. Segments in polymer chains that are linked together by secondary valence bonds act like crosslinks. The areas between these weak crosslinks in the polymer chains can be stretched by a brief tensile force. When the force is released, the chains return to their original shape. However, if the force acts for a protracted period of time, the secondary valence bonds undergo re-orientation. This causes the polymer to lose its original shape.

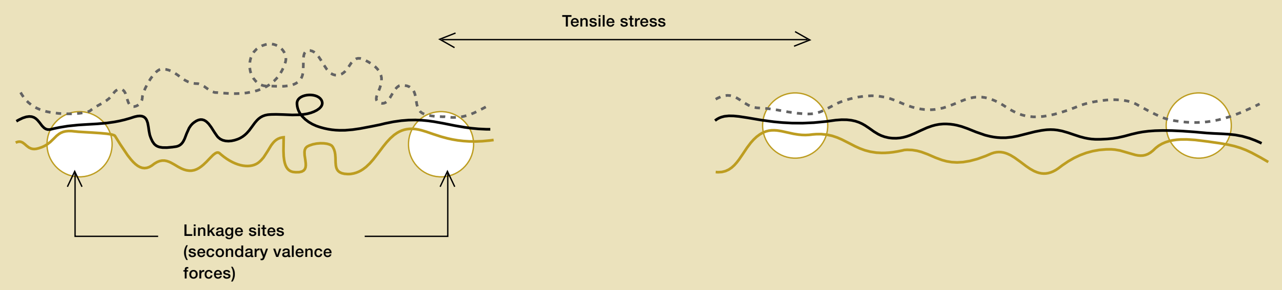
WACKER® BOUNCING PUTTY, a silicone polymer from WACKER is a particularly good example of the properties of viscoelasticity. A sample that has been made into a ball will slowly start to flow and will ultimately turn into a flat disk. When exposed to large forces, bouncing putty behaves like an elastic material with very high rebound elasticity: a ball thrown against the ground will bounce to a height equivalent to what would be expected if it had been thrown two or three times as hard.

If exposed to a very high force, bouncing putty behaves like a brittle glass. For example, if a ball of it is hit with a hammer, the impulses that occur on impact smash it into small pieces.

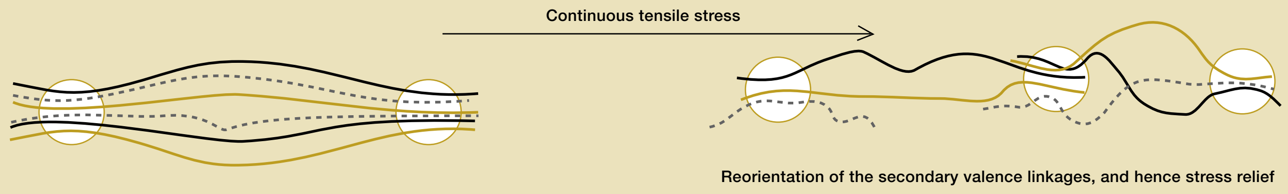
This phenomenon may be explained in terms of the structure of the polymer contained in bouncing putty. It consists of not only the typical siloxane chain links, but also boroxane groups (approx. 0.5 mol %), which consist of boron and oxygen atoms (every fifth to 100th silicon atom is replaced by boron). Because boron is more electropositive than silicon, the atoms of the boraxane units display electric charges – negative for oxygen and positive for boron. If an external force compels two chains to approach each other, electrostatic

Elasticity and viscoelasticity in polymers

Elastic behavior of a polymer



Viscoelasticity of the bouncing putty



forces of attraction come into play and a crosslinking site is formed. The greater the force, the more crosslinking sites are formed, which in turn leads to the phenomenon of elastic or brittle-elastic behavior. However, the bonds between these crosslinking sites are so weak that even thermal motion in a pressureless state is sufficient to break them. In the case of bouncing putty, we are dealing with enforced crosslinking under exposure to a force, which disappears again when the force is removed.

Bouncing putty is mainly used for therapeutic purposes. It is ideal for strengthening arm muscles because when kneaded with the hand it puts up the same amount of resistant force as is applied in trying to knead it.

E9.2 Exercises Involving WACKER® BOUNCING PUTTY 29

If you make a ball out of WACKER® BOUNCING PUTTY 29 and let it bounce, it will not change its shape (exposure to rapid forces). If you throw it against a wall with enough force it will bounce back to twice or three times the distance.

A ball of RTV-2 silicone rubber left for a long time, however, will liquefy to form a pancake-shaped disk. Similarly, it can be kneaded to a different shape in the hand.

If, however, a large force acts on it, it offers greater resistance to this deformation. For this reason, WACKER® BOUNCING PUTTY 29 is used as a kneadable compound in medical rehabilitation for training and building up muscles.

If the WACKER® BOUNCING PUTTY 29 is divided into two (which is not so easy!) and the two pieces are brought into contact with each other, they instantaneously fuse together again.

E10 ADHESIVES FOR ALL PURPOSES

Chemicals from the school laboratory:
Casein powder
NaOH

ADHESIVES FOR ALL PURPOSES

E10.1 What are Adhesives? Properties

Definition of an adhesive

An adhesive is a non-metallic substance capable of holding component parts (adherents) together by surface attachment (adhesion) and internal strength (cohesion) without causing major changes to the structure of the materials.

One way of classifying adhesives is on the basis of physical and chemical reaction. Physically setting adhesives (glue, paste, and solvent-based, emulsion-based and hot-melt adhesives) may or may not contain solvent. They effect a join by undergoing a change in physical state (liquid → solid) as when a melt cools down or by evaporation of a solvent before and during the bonding process. They generally consist of one component.

Chemically setting adhesives (cyanoacrylate, urethane, epoxy) may consist of one or more components. These reactive adhesives utilize all types of polymerization (polyaddition, polycondensation, epoxy resin etc.). They are thus capable of bonding nearly all materials. The predominant goal of current research into adhesives is to replace solvent systems with solventless systems or systems that contain water as solvent. This changeover is necessary for ecological and economic reasons. Another way of classifying adhesives divides them into natural and synthetic types. Natural adhesives are subdivided into those derived from animals (glutin glues, casein glues), plants (starch, dextrin, natural rubber) and minerals (waterglass).

Historical background on adhesives

As long ago as 5,000 BC, neolithic man used birch resin as a natural adhesive for attaching arrowheads to spears and harpoons. Around 4,000 years ago, the Sumerians discovered, probably by accident, that a sticky gelatinous mass was formed when animal skins and bones were boiled together and that it could be used to join pieces of wood together. This was the first glutin glue. Glutin is a gelatinous, viscous compound that is generated by boiling collagens (the protein contained in connective tissue), cartilage and bones. The Sumerians may also have used asphalt as a binder when building their houses and temples. In the pre Roman era, adhesives based on albumin (blood protein) and hemoglobin, etc. were used. When the grave of the Egyptian king Tutankhamen, who lived around 1,300 BC, was discovered, among the burial objects was a lump of glue. This find proved that an adhesive was considered something important and valuable back then.

Down the centuries and continuing through the present day, the following materials have been in use:
gelatins, blood, alginates, shellac, gum arabic, agar-agar, resins, balsam, bitumen and waxes.

Case study:
Natural products for dispersions (casein as binder in paints and gelatins as adhesive)

Theoretically, biological products may serve as substituents for adhesive dispersions and binders for interior paints. For instance, casein, a renewable raw material, could serve as a binder substitute. The problem lies in the quantities required:
Milk contains only 2.8 - 3 % casein. The average, high-yield dairy cow produces 5,000 kg of milk each year, or roughly 145 kg of casein. Since casein is not a strong binder, typical casein recipes must contain up to 25 % casein. To replace the annual German production of 80,000 metric tons of dispersions, roughly 1.25 million cows would be needed – just to produce the casein binder. Such a large number of cows would pose a serious threat to our environment. Using casein as a substitute would literally mean daubing walls with the most nutritious part of milk, namely protein. In addition, casein paints are not exactly cheap (approx. EUR 5/kg casein compared with EUR 1.50/kg for PVAC).

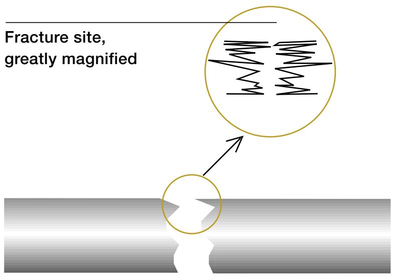
Experiment: The Glue of the Ancient Egyptians

Making a casein glue:
Casein is the protein contained in mammal's milk and is a white powder that is insoluble in water and soluble in alkalis. Dissolve 10 g casein powder in 25 ml dilute NaOH and allow the suspension to swell for a few minutes. Now try to use this glue to stick various materials together, e. g. two pieces of wood, glass microscope slides, paper, and small plastic strips. Use a clothes-peg to pin the joined areas together until the glue has dried. Which materials adhere strongly to each other? Which do not?

The bonding process

Bonding is the joining together of similar or dissimilar materials by means of an adhesive. Setting is the process by which the liquid adhesive layer solidifies. But how does bonding work and which processes allow two adherents to be joined together?

A broken glass rod



Fracture site in a broken glass rod

If the ends of a broken glass rod are squeezed tightly together, it very soon becomes apparent that no matter how much force is used that they cannot be joined. Why is this?

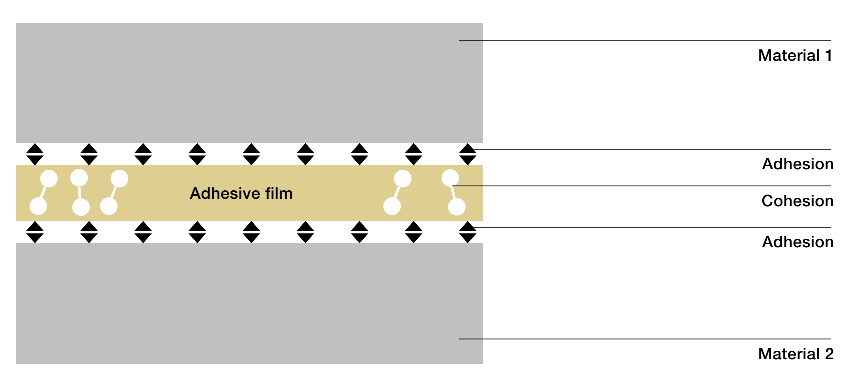
Before two surfaces can be joined firmly together, two conditions must be fulfilled:

1. There must be forces of attraction between the particles of the two surfaces.
2. In order for these forces to act, opposing particles must be as close to each other as possible; the distance between them must not be greater than 10^{-12} - 10^{-9} meters. Normal techniques are unable to meet this condition for broken surfaces.

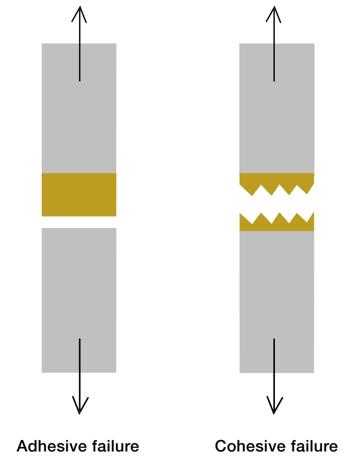
There are basically two ways in which the two ends of the glass rod can be joined firmly together. One is to melt them so that the glass liquefies and the particles can get close enough together to allow the forces of attraction to act. The other is to use a liquid agent – adhesive – that hardens in contact with both surfaces.

The three most important requirements are therefore: the adhesive must be liquid or at least pasty during application, it must bond to the adherents and it must have adequate inner stability. These last two properties are called adhesion and cohesion. They are the two key concepts in the adhesives industry and they explain why and how effectively materials bond together.

Adhesion and cohesion, the key concepts in bonding



Failure at a bonded joint



Adhesion is the sticking of the adhesive layer to the surfaces of the adherents; i. e. the interaction between the adhesive and the surface of the materials to be bonded.

Adhesion can occur through
- The formation of intermolecular forces in the interface region, e.g. van der Waals forces or hydrogen bonds
- The formation of chemical bonds between adhesive molecules and surface molecules
- Interlocking of polymer molecules and reactive layers of the material surface at a microscopic level
- Diffusion by the molecules in the adhesive layer and adherents in the interface region
- Wetting forces in the interface region

Cohesion is the internal strength of an adhesive. It describes the interaction occurring within a material.

Cohesion is influenced by
- The physical state
  (it is most effective in a solid)
- The molecular weight and the functional groups
  (high interaction = great cohesion)
- The arrangement of the polymer tangles, i. e. crosslinking
- The temperature (the higher the temperature, the lower the cohesion)

When a bonded joint fails, adhesive and cohesive failure can therefore be identified as shown above.

WACKER supplies a wide range of polymer dispersions. (not included in the experimental kit).

LIST OF CHEMICALS

Chemicals from the experimental kit

Experiment	Chemical	Physical form	Other experiment	Quantity
V1 Viscosity V1	WACKER® SILICONE FLUID AK 1000	Liquid	E2, E7	30 ml
V1 Viscosity V1	WACKER® SILICONE FLUID AK 5000	Liquid	E2, E7	30 ml
V2 HDK®	HDK® N20 hydrophilic fumed silica	Powder	E2	7 g
V3 Defoaming	SILFOAM® SRE	Liquid		20 ml
V4 Impregnating	SILRES® BS SMK 1311	Liquid		30 ml
V5 Paper coating	DEHESIVE® 920, silicone release agents	Liquid		100 ml
V5 Paper coating	WACKER® CROSSLINKER V 24	Liquid		5 ml
V5 Paper coating	WACKER® CATALYST C 05	Liquid		5 ml
V6 Mold making	ELASTOSIL® M 4601 A, mold-making compound	Liquid	E8	200 ml
V6 Mold making	ELASTOSIL® M 4601 B, mold-making compound	Liquid	E8	20 ml
V6 Mold making	ELASTOSIL® M 4400, mold-making compound	Liquid	E8	100 ml
V6 Mold making	WACKER® CATALYST T37, catalyst for mold-making compound	Liquid	E8	10 ml
V7 Jointing	ELASTOSIL® E 43 transparent	Paste		30 ml
V8 Property of silicone rubber	RTV slabs			3 slabs
V9 Bouncing putty	WACKER® BOUNCING PUTTY 29	Kneadable compound		30 ml

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Notes:

WACKER AT A GLANCE

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With R&D spending at almost 6 % and capital expenditures at 13 % of sales, WACKER is among the top research companies worldwide.

Siltronic
is one of the world's leading producers of hyperpure silicon wafers, supplying several major chip manufacturers. Siltronic develops and supplies wafers up to 300 mm in diameter at facilities in Europe, the USA, Asia and Japan. Wafers made from hyperpure silicon form the basis of state-of-the-art microelectronics used, for example, in computers, telecommunications, motor vehicles, medical technology, consumer electronics and control systems.

WACKER SILICONES
is one of the world's leading silicone producers. With a portfolio of over 2,000 products, this division is number one in many global markets. Silicones are the basis for materials offering highly diverse product properties for virtually unlimited applications. These are found in a broad range of industries from the automotive, construction and chemical sectors, through electrical engineering, electronics, cosmetics, consumer care, pulp and paper, and textiles, to mechanical engineering and metal processing.

WACKER SPECIALTIES
is the global leader for high-quality binders and polymer additives. Products such as re-dispersible powders, dispersions, solid resins, powder binders and surface coating resins are used in the construction, automotive, and paints and coatings industries, as well as by manufacturers of printing inks. Additionally, this division has expertise as a provider of customized fine-chemical and biotechnology solutions, including building blocks for syntheses in the pharmaceutical, cosmetic and agrochemical industries.

WACKER POLYSILICON
has been producing hyperpure silicon for the semiconductor and photovoltaics industries for over 50 years. As one of the largest global manufacturers of polycrystalline silicon, WACKER POLYSILICON supplies leading wafer and solar-cell manufacturers.

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