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SILICONES IN PROTECTION OF CONSTRUCTION MATERIALS

Introduction

Silicon is an element found in the Earth's crust in the amount of 27.6%. It is a main ingredient of rocks where it is found in the form of silicate or silicon-dioxide. Specific characteristics of silicon, located in the middle of the fourth group of Periodic Table of Elements between metals of the fourth group and metalloid carbon, conditioned the chemistry of silicon-organic compounds. Compared to organic, carbon compounds, silicon-organic compounds can't be found in nature, they are exclusively synthetic products. The chemistry of silicone developed very fast, and one of the reasons is the reduction of natural resources necessary for organic chemistry (oil, coal) or their limited production (natural plant polymers). Fast development of silicone was also enabled by the knowledge (methods, reactions, apparatus and technology) used according to analogy, and it stems from organic chemistry.

Nomenclature of silicon-organic compounds is also done according to the analogy of names of appropriate organic compounds. The very term silicone is derived from the name ketone.

>C = O	>Si = O
ketone	silicone

Due to their specific characteristics these nonorganic-organic compounds find their purpose very fast, even though their application was very late in some cases, or is still legging behind the science. A great number of patents exclusively relates to the use of silicone.

Silicon-organic Monomers

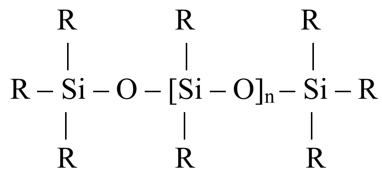
Theoretically it is possible for a silicon atom to become attached to any organic compound, which is mostly proven in practice, and that explains a huge number of compounds of this type. The number of silicon-organic monomers increases by a possible attachment of another element (except carbon) to silicon.

The greatest number of silicon-organic monomers is known under the name **silanes.** Silanes are nowadays used as ready-made products in various areas of industry. Many of these products have not been used yet, and consequently their importance is only scientific, or they represent raw materials for the provision of other types of silicon-organic compounds.

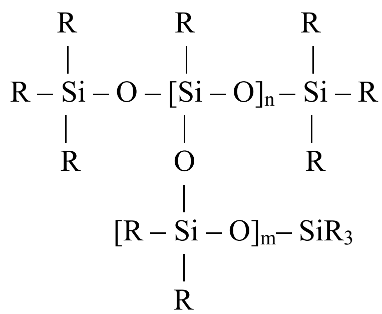
   |
[–Si–O–]$_n$ silanes
   |

Olygosiloxanes

Olygosiloxanes are compounds made of non-organic skeletons and an organic part attached to silicon. Organic part could be alkyl or aryl radicals.
The most widespread products are olygoalkylsiloxanes. Olygoalkylsiloxanes can be linear and branched.



linear



branched

where R = alkyl group

Olygomethylsiloxanes are produced by balancing dichloro and monochlorsilane hydrolysates. Reactions are catalyzed by proton catalysts. The length of siloxane chain is regulated by the amount of monochlorsilane which has the role of a blocker. After equilibration finished products are being separated from the mixture. The products are flowable and commercially known as **silicone oils**.

Methylsilicone oils have exceptional physical-chemical characteristics and consequently an extensive use. Oxidational and thermal stability of these oils are good. Oils are stable to oxidation in air up to 150^{o}C, and without the presence of oxygen up to 200^{o}C. They do not corrode metals. They are degraded by strong, concentrated mineral acids and strong heated alkali. If it is known that methylsilicone oils have a high ignition temperature on air (320^{o}C), high spontaneous ignition temperature (around 450^{o}C), low pour point (around -50^{o}C), high dielectric strength (around 250KPa/cm^2) and other positive characteristics, it is clear that these oils are extraordinary thermal liquids (heating aggregates, oil baths, thermostats) and dielectric cooling liquids (oils for transformers and capacitors).

Methylsilicone oils are very compressible and stable at high pressures. Upon compression viscosity increases, but solidification pressures are a lot higher comparing to mineral oils. This characteristic, as well as a quite small change of viscosity with the change of temperature, enables silicone oils to be used as amortizing, braking, compression and hydraulic liquids.

Other characteristics of methylsilicone oils, such as health safety, water repellency, good lubrication, low surface tension were used in the application of methylsilicone oils or products based on these oils, such as:

- defoamers,
- lubricating liquids,
- medical products (silicone oils are injected into the vitreous body of the eye, where drinking water would cause catastrophic consequences),
- additives for cosmetic and dermatological products,
- additives for colors and lacquers,
- additives for polishes,
- waterproofing products (high voltage insulators, surgical instruments, glass),
- in aesthetic surgery.

Silicone oils, which contain aryl instead of alkyl groups, or contain both groups, have other noticeable qualities, and consequently a different use.

Compounds where a silicone polymer is attached to other organic polymer are silicone co-polymers. Co-polymers are applied in many branches of industry. Somewhere the application of co-polymers is so important that a branch of industry cannot be imagined without them.

A group of compounds and corresponding commercial products, such as co-polymers, belong to extremely effective emulsifiers that are massively used in the cosmetics industry.

Heterosiloxanes

Organic-silicon compounds which contain group Si-O-M, where M is any metal or non-metal, are called **heterosiloxanes.** Heterosiloxanes are important in the theory of chemistry as chemical agents, and their use as ready made products has recently started. I am pointing out to some examples from a big group of compounds which are used.

Alkylsiloxanes of alkali metals with zinc salts produce compounds that are not much soluble and are used for hydrophobing of textile.

Besides water repellency and anti-static effect, upon processing textile with zincorgansiloxanates there is also germicide effect.

Boron heterosiloxanes are applied in microelectronics, as catalysts for epoxide resin, as products for the increase of thermal stability of synthetic rubber and so on.

Aluminium heterosiloxanes are used for hydrophobing textile, as catalysts for polyethylene synthesis, for catalysis and synthesis of organic compounds.

Tin heterosiloxanes are used for the production of plastic masses, compounds, lacquers.

Titanium heterosiloxanes are used as additives against thermo-oxidational destruction, as catalysts, in the production of elastomers, compounds, lacquers, absorbents.

Lead heterosiloxanes are used as stabilizers of polyvinyl resin.

Silicones in construction

Silicone elastomers are a big group of polymer compounds of silicone rubber and silicone caoutchouc. Vulcanization of silicone rubber can be done in cold environment: **RTV** silicone rubber (**R**oom **T**emperature **V**ulcanization - vulcanized at room temperature) and in warm environment: **HTV** silicone rubber (**H**igh **T**emperature **V**ulcanization - vulcanized at high temperature). Silicone rubber vulcanized in cold environment is well known and very important from the perspective of construction industry. It is used as protective material, and after vulcanization it becomes elastomer and can be defined by demonstrating a range of needed characteristics:

- high or low modulus of elasticity,
- good adhesion,
- high steam permeability,
- paintable,
- resistance to UV radiation,
- excellent flexibility in the range from -50°C to 300°C.

RTV silicone sealers can be either acid or neutral depending on the crosslinker. The basis for all these sealers are α,ω-dihydro(poly)-dimethylsiloxane:

$$HO - [\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}} - O]_n - H$$

which together with crosslinkers produce an elastomer through the reaction of polycondensation.

Ready-made product also contains accelerators, fillers, pigments etc. Lately there has been a huge number of producers of silicone putty. Many producers create silicone putties mixed with acrylates, which is why it is necessary to read declaration before the purchase.

Effects of water and humidity on construction materials

Water as a universal dissolver attacks all construction materials dissolving more or less its integral components. Atmospheric water, other types of water and humidity get into the pores of every material regardless of its porousness. Porousness of the material only affects the quantity of water and the depth it penetrates under certain conditions. Dissolving construction material water expands its pores making the material lose its basic characteristics. The final effect of water is decomposition - a complete destruction of construction material.

Wet construction material at low temperatures freezes, water in pores freezes and starts expanding, which leads to important changes in the structure of material and finally to cracks on buildings.

Water which remains in the construction material turns into water vapour at high outdoor temperatures. During evaporation water expands and water vapour pressures damage construction material.

Upon slow evaporation of water a repeated salt crystallization occurs in the construction material. Crystallization pressures are extremely high, leading to the destruction of construction material.

Trebinje, Serbian Orthodox Temple (balcony, South and North facade): damages on the stone

A part of dissolved material is brought to the surface by water. After water evaporation these minerals are left on the surface of construction material in the form of amorphous precipitate - white or grey powdery stains or layers. This phenomenon is known as salting out of construction material.

Atmospheric water can be occluded with different impurities from atmosphere such as carbon-dioxide, sulphurous and nitrous oxide, dust, soot etc.

Carbon-dioxide dissolved in water is carbon acid which causes deterioration of construction material and buildings:

$$\underset{\text{water}}{H_2O} + \underset{\text{carbon-dioxide}}{CO_2} \rightarrow \underset{\text{carbon acid}}{H_2CO_3}$$

If there is humidity in atmosphere, sulphurous and nitrous oxides are transformed into corresponding acids causing acid rain:

$$\underset{\text{water}}{H_2O} + \underset{\text{sulphur-dioxide}}{SO_2} \rightarrow \underset{\text{sulphurous acid}}{H_2SO_3}$$

$$\underset{\text{water}}{H_2O} + \underset{\text{sulphur-trioxide}}{SO_3} \rightarrow \underset{\text{sulphuric acid}}{H_2SO_4}$$

$$\underset{\text{water}}{H_2O} + \underset{\text{nitrogen-trioxide}}{N_2O_3} \rightarrow \underset{\text{nitrous acid}}{2HNO_2}$$

$$H_2O + N_2O_5 \rightarrow 2HNO_3$$

water nitrogen-pentoxide nitric acid

Acid rain constantly damages constructions.

Belgrade, Monument in the honour of Belgrade defenders 1914-1918: salting out of construction material

Due to impurities in the atmosphere constructions get dirty very fast. Today, all these phenomena are a lot more evident than fifty or a hundred years ago when the atmosphere was much cleaner.

Construction materials are also attacked by various organisms: lichen, fungus, algae, mould and moss. These organisms use construction material as their habitat, food or both. Their life mostly depends on water (humidity) in construction material.

Zemun, Saint Father Nikolaj Temple: moss and lichen on a stone vase

It is little known that certain types of water algae can penetrate so-called “Gelcoat”, the smooth, protective surface layer of polyester resin in a fiberglass structure of navigable vessels and consequently destroy yachts and boats.

Larvae of some insects attack wood and use it as food. Classical anti-larval products (fungicides, insecticides) are mostly poisonous, both to humans and larvae. Fortunately, the time of evaporation or dissolution of these products is short.

Due to wetting and drying, spreading and shrinking of wood cause the appearance of cracks leading to possible rotting and decay.

Iron, copper, aluminum and their alloys are the materials extensively used in construction industry. Water and humidity from air affect metals and damage them.

Iron gets corroded in touch with humidity, building the black and dark-ginger colored oxides:

$$2Fe + 2H_2O \rightarrow 2Fe(OH)_2 \rightarrow \underset{\text{black}}{2FeO} + H_2O$$

$$4Fe(OH)_2 + O_2 \rightarrow \underset{\text{dark-ginger}}{2Fe_2O_3} + 4H_2O$$

If there is humidity in the atmosphere, copper and copper alloys (brass, bronze) create light-green soluble copper-hydrogencarbonate (copper-bicarbonate):

$$
\begin{array}{ccccccccc}
 & & 4CO_2 + 4H_2O & & & & & & \\
 & & \downarrow & & & & & & \\
2Cu & + & 4H_2CO_3 & + & O_2 & \rightarrow & 2Cu(HCO_3)_2 & + & 2H_2O \\
 & & \text{carbonic acid} & & & & \text{light green} & &
\end{array}
$$

Copper-hydrogencarbonate commonly appears in the form of light-green stains on the facades of buildings with copper roof or gutters.

Protective silicone products

Serious construction damages are caused by the effect of water. Therefore, protecting constructions from water and humidity is an imperative respected worldwide and regulated by the law.

All around the world silicone products used for the protection of constructions from water and humidity are well known and unequalled for the time being. The production of protective water-repellent silicones is very important and quite huge in quantity with famous global giants such as: **Dow Corning**, **Rhone-Poulenc**, **Bayer** etc.

There are many silicone products used for achieving water-resistance of a material and they are categorized by the type of compounds and product formulation. Generally speaking, hydrophobing of almost all materials (not just those in construction) is done by the greatest number of silicone products which includes monomers and polymers where hydrogen is attached to silicon:

$$
\begin{array}{c}R\\|\\C_1\text{–}Si\text{–}S\\|\\H\end{array}, \quad
\begin{array}{c}R\\|\\R'O\text{–}Si\text{–}OR'\\|\\H\end{array}, \quad
\begin{array}{c}R\\|\\[\text{–}Si\text{–}O\text{–}]_x\\|\\H\end{array}, \quad
\begin{array}{c}R\\|\\[\text{–}Si\text{–}NH\text{–}]_x\\|\\H\end{array}
$$

etc.

Ready-made products to be used in construction are present on the market mostly as dissolved polymers - silicone resin, or as water-based systems which become water-resistant on air. These silicone-polymers get attached to construction material by adhesion and consequently the material itself becomes water-resistant. Water-resistance of silicone-polymers is created as a consequence of water-resistance of radicals that are attached to silicon. This characteristic depends on the construction of polymer: the type of radical, degree of special networking and functional groups which are, besides radicals, attached to silicon.

Zemun, Saint Father Nikolaj Temple: stone vase and capital after cleaning, restoration and conservation and vase and capitals which were not treated (in the backround)

Within its production program of silicones **Hemi Eco** company takes special care of silicone products for the protection of construction buildings and construction materials, and emphasizes them as its specialty. A range of **Hemi Eco** products can be used to protect all commonly used construction materials: stone, artificial stone, all types of brick and ceramics, mortar, concrete, plaster, metal, glass and others.

Materials from our production program have following characteristics:

- Size and characteristics of silicone molecules are adjusted to the type of construction material intended for protection, i.e. to the porousness and chemical composition of construction material,
- Silicone-polymer is created in the structure of material which is being protected,
- Relatively small silicone molecules enable deep penetration into construction material and consequently efficient protection,
- Degree of spatial networking of polymers is the highest possible,
- Construction material protected with **Hemi Eco** products changes neither colour nor appearance, and some positive characteristics are improved (for example hardness),
- Extraordinary durability - anti-aging effect,
- Achieved water-resistance of a building eliminates negative effects of water, from soiling to deterioration, as well as the appearance of mould, lichen and fungi,

- Anti-static effect of **Hemi Eco** silicones prevents a building from becoming electricity charged,
- Water which somehow penetrates conserved material freezes at temperatures below -100^{o}C.

Laboratory brick models: standard model and conserved sample

Laboratory brick models after a six-month long exposure to humidity:
standard modeland conserved sample

Laboratory brick models: standard model and conserved sample

Laboratory brick models after 30 freezing-melting cycles: standard model and conserved sample

I would like to single out some more products based on silicones:

- Protective anti-graffiti silicone products are very important. No matter how professionally removing of graffiti is done, it still damages the construction. Construction protected with a high quality silicone product can simply be washed with water after it was painted or sprayed with color.

- Fire protection materials based on silicones, used for the protection of wood, also exist. Silicone combined with other materials provides wood with water-resistance, and in case of a fire it is decomposed to CO_2, H_2O and SiO_2. Silicon-dioxide is an exceptional fire protection material which remains in the wood and prevents it from burning.

- According to their composition, special protective materials are 100% silicones. After applying, silicone enters material structure and after vulcanization it provides it with complete water-resistance and water-impermeability at high pressures (examined at 8bar). Health safety of the material enables its broad application.

- Water-based silicone systems can be added into mortar and concrete for the purpose of reparation, as well as in mortar and concrete that need to be water-resistant and water-impermeable.

- Classic waterproofing products based on bitumen can be significantly improved if bitumen is combined with silicones to make special copolymers. Such products have great durability, elasticity at low temperatures, water-resistance and water-impermeability.

R e s u m e

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SILICONES

The exceptionally fast development of the chemistry of silicones enables their widespread use in various fields of science, industry, medicine and engineering. The manufacturing of silicone is thus constantly on the rise, not only because of the growing use of the already well known silicone products, but also because of the new products of ever improving quality whose performances are almost unbelievable. In the words of the makers of one new product: "The improvements in the patented ENGINEERING SILOXANE are even more fundamental than the patent itself and require a reworking of the Periodic Table of Elements".

Belgrade, 2007