

SYNTHETIC BASICS

Silicone Fluids: Synthesis, Properties and Applications

P. Huber and W. Kaiser Wacker-Chemie GmbH, W. Germany

This paper describes the structure and derivation of 'classical' silicone fluids, giving the reactions for the production of dimethyl fluids by Müller-Rochow synthesis, polymerisation, direct synthesis, hydrosilylation, and transesterification. The properties of siloxanes are described, and the applications of silicone fluids and compounds are discussed in relation to their properties, particularly insolubility in water, viscosity-temperature characteristics, and dielectric properties.

Generally, the term 'silicones' refers to oligomeric or polymeric organic silicon compounds, where silicon atoms are linked together by oxygen so that alternating Si—O—Si bonds are obtained as the backbone.

Structure units (Figure 1) can be drawn for the compounds. The monofunctional groups (the so-called end-groups) of the organo-poly-siloxane molecule limit the chain length, the degree of polycondensation and thus the viscosity of the polymer.

The difunctional units form rings or higher-molecular chains, whereas the tri- or tetrafunctional units lead to three-dimensional crosslinked systems.

This paper will mainly deal with the mono- and difunctional siloxane units, as these structures represent the main components of the linear polysiloxanes, ie the 'liquid silicones'.

These silicones liquids, represented in the general formula shown in Figure 2, can be modified by the parameters R, R' and index x .

R' can be a reactive group, ie OH, H, Alkoxy ($\text{CH}_3\text{O} \rightarrow \text{C}_{18}\text{H}_{37}\text{O}$ or $\text{C}_6\text{H}_5\text{O}$), Acyloxy (CH_3COO) or a non-reactive group such as methyl, alkyl or aryl. However, here, with the emphasis on silicone liquids as base fluids for lubricants and operational fluids, we will not consider

Figure 1 Structures for compounds

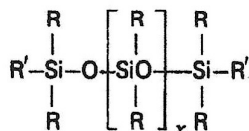
Type	Molecular formula	Structure	Starting silane
Monofunctional	$R_3SiO_{1/2}$	$\begin{array}{c} R \\ \\ R-Si-O- \\ \\ R \end{array}$	R_3SiCl
Difunctional	$R_2SiO_{2/2}$	$\begin{array}{c} R \\ \\ -O-Si-O- \\ \\ R \end{array}$	R_2SiCl_2
Trifunctional	$RSiO_{3/2}$	$\begin{array}{c} R \\ \\ -O-Si-O- \\ \\ O \\ \end{array}$	$RSiCl_3$
Tetrafunctional (quaternary)	$SiO_{4/2}$	$\begin{array}{c} \\ O \\ \\ -O-Si-O- \\ \\ O \\ \end{array}$	$SiCl_4$

variations of the reactive groups but concentrate on the classical silicone fluids with non-reactive end-groups.

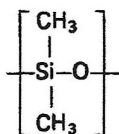
Organosiloxane liquids are classified according to the substituent R. More than 90% of the organopolysiloxanes are built up from dimethylsiloxane units (Figure 3) and the trimethylsilyl-terminated dimethylpolysiloxanes (Figure 4) represent the most important group of silicone fluids.

The siloxane chain therefore consists of dimethylsiloxane groups and is terminated by trimethylsilyl endgroups. The chain length of such molecules may be adjusted by the proportion of M- to D-units; that means the proportion of mono- to difunctional units.

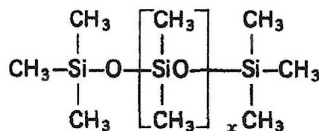
As shown above, the index α relates the viscosity of the product with its molecular weight. We should add, that except for the lowest,

Figure 2 General formula of silicone fluids

R' can be: Alkyl, OH, H, Alkoxy, Acyloxy, R
 R can be: CH₃, Alkyl, Aryl

Figure 3 Dimethylsiloxane

as difunctional unit

Figure 4 Trimethylsilyl terminated dimethyl polysiloxanes

$x = \sim 0\text{--ca. } 2000$

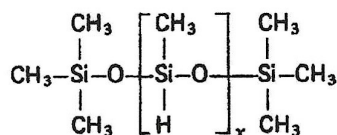
viscosity = 0.65–1,000,000 mm²/s

still distillable members, all members of this homologous series show a molecular weight distribution.

Another very important group of silicone fluids is represented by the so-called methylhydrogensiloxanes (shown in Figure 5). In this case, one methyl group of the difunctional units is substituted by a hydrogen atom. The commercially available products of this type can roughly be described by index x as well as by the given viscosity range.

In the case of the phenylsilicone fluids, more precisely phenylmethyl-silicone fluids (Figure 6), methyl groups of the usual polydimethyl-siloxane backbone are substituted by phenyl groups. Variations of the

Figure 5 Methylhydrogenpolysiloxane

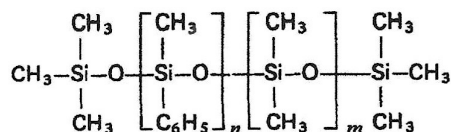


$$x = 40-90$$

$$\text{viscosity} = 15-100 \text{ mm}^2/\text{s}$$

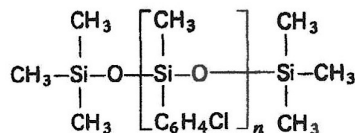
Figure 6 Phenylmethylpolysiloxane

Phenylmethyl-silicone fluids



$$\text{viscosity up to } 10,000 \text{ mm}^2/\text{s}$$

Chlorophenylpolysiloxane

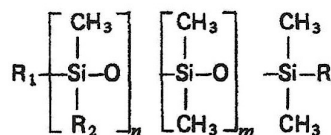


physical-chemical characteristics can be achieved by modifying the proportion n/m as well as by a substituent on the phenyl groups, as can be seen by the example of the chlorophenylsiloxanes.

In the course of the last fifteen years numerous modified siloxanes (Figure 7) have appeared on the market in addition to the classical polydimethylsiloxanes. Due to the large variety of possibilities, substantial modifications of the polydimethylsiloxane characteristics can be achieved, so that these products are successfully used as speciality products in relatively well defined applications.

Finally, we should mention a further modification, which already has been produced in large quantities by silicone manufacturers, namely the glycolfunctional siloxanes (Figure 8). Usually, in these compounds, which in many cases are water-soluble, glycol chains consisting of ethyl-

Figure 7 Modified silicone fluids



R₁ can be: methyl, hydroxyl, vinyl

R₂ can be: alkyl with 2-18 C atoms

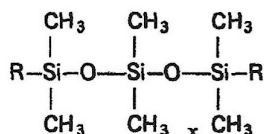
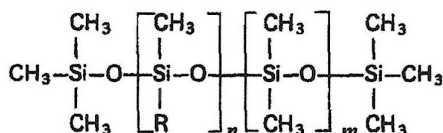
alkylaryl
fluoroalkyl
vinyl

aminoalkyl: $-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_2\text{NH}_2$

or $-(\text{CH}_2)_3-\text{NH}_2$

mercaptoalkyl: $-(\text{CH}_2)_3-\text{SH}$
$$\text{epoxyalkyl: } -(\text{CH}_2)_3-\text{O}-\text{CH}-\text{CH}_2$$

Figure 8 Polyether-polysiloxane copolymer



R can be: polyoxyethylene unit $[\text{CH}_2\text{CH}_2\text{O}]_y-\text{R}_1$

$$\text{polyoxypropylene unit } \left[\begin{array}{c} \text{CHCH}_2\text{O} \\ | \\ \text{CH}_3 \end{array} \right]_{l_v} \text{---R}_1$$
 $-(CH_2)_3-$ polyoxyethylene $-(CH_2)_3-$ - polyoxypropylene

R_1 can be H or CH_3CO alkyl

eneoxide and/or propyleneoxide units are grafted onto the linear siloxane backbone.

In many cases, the nature of the linkage is decisive for use in aqueous systems. Linkage is possible via a Si—O—C bond which can be hydrolysed, or by an unsaponifiable Si—C bond.

PRODUCTION OF SILICONE FLUIDS: TYPICAL REACTIONS OF ORGANO-SILICONE CHEMISTRY

A few fundamental reactions are of major importance and characteristic of organo-silicone chemistry, in this case mainly for the production of dimethyl fluids.

Firstly, methylchlorosilanes, which economically represent by far the most important group, are produced according to Müller-Rochow synthesis. The desired product, dimethyldichlorosilane, is obtained according to the equation and method shown in Figure 9, where the basic materials, silicon and gaseous methylchloride are converted by means of a copper catalyst, usually in a gas/solid reaction at about 260–320°C.

Hydrolysis or methanolysis of the corresponding organochlorosilanes followed by condensation are consecutive steps of the silane synthesis. The acid chloride of the silicic acid or their organic derivatives reacts with H₂O or methanol. The reactions are described for dimethyldichlorosilanes in Figure 10, which also shows the subsequent condensation reaction, ie transformation of the silanol groups, obtained by hydrolysis, into higher molecular siloxanes by eliminating water. A problem is the considerable quantity of HCl liberated by the hydrolysis reaction. Methanolysis therefore represents a more economical and an ecologically more favourable procedure as the chlorine can be recycled as methylchloride.

Another important type of reaction is the polymerisation reaction (Figure 11), ie the conversion of siloxane rings free from hydroxyl groups into higher molecular linear polysiloxanes.

The equilibration reaction (Figure 12) is of major importance in the preparation of silicone fluids. The aim of this reaction is to homogenise a non-homogeneous siloxane mixture of varying molecular weight distribution by means of catalysis in such a way that the final product exhibits a Gaussian molecular weight distribution. This reaction is mainly used for the production of silicone fluids in order to obtain a desired uniform distribution of the *m*-units and thus to obtain a specific chain-length and so the required viscosity range.

These reactions represent the most important chemical procedures for the production of standard silicone fluids, ie polymethylsiloxanes endblocked by the corresponding *m*-units. Phenylsilicone fluids and glycol-modified fluids are made using different reactions.

Figure 9 Gas/solid catalyst reaction

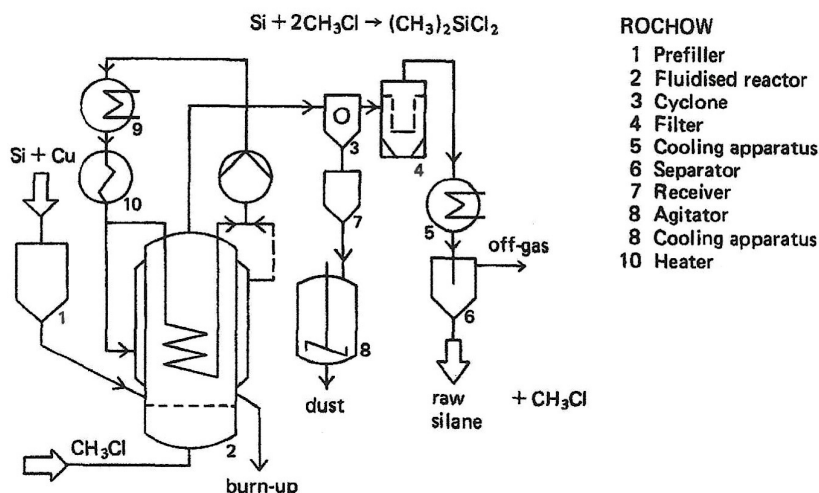
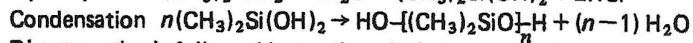
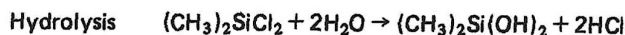
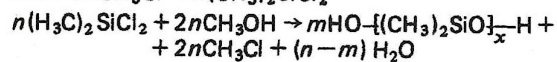
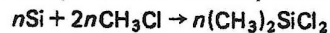


Figure 10 Hydrolysis and methanolysis reactions and condensation



Direct synthesis followed by methanolysis:



$$m \cdot x = n$$

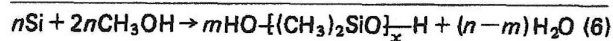


Figure 11 Polymerisation reaction

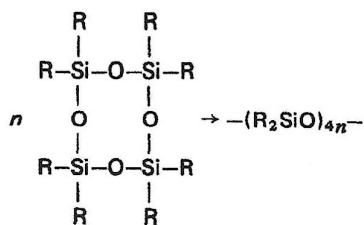
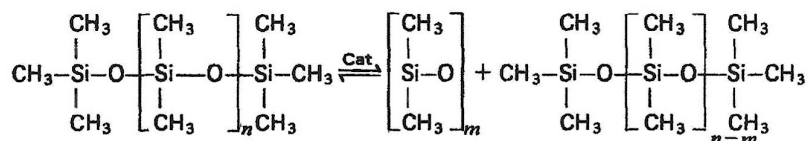


Figure 12 Equilibration reaction



ca. 10-15% cyclic siloxane linear chains

Figure 13 Direct synthesis

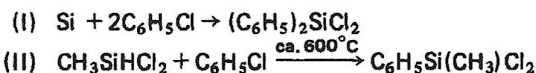


Figure 14 Hydrosilylation reaction

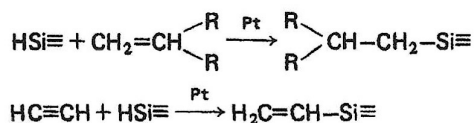
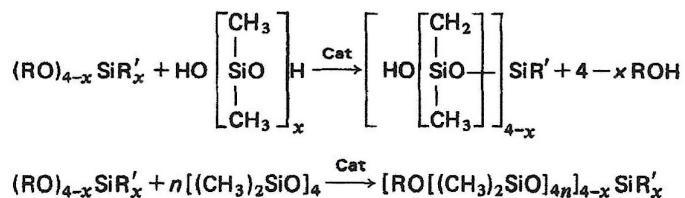


Figure 15 Transesterification

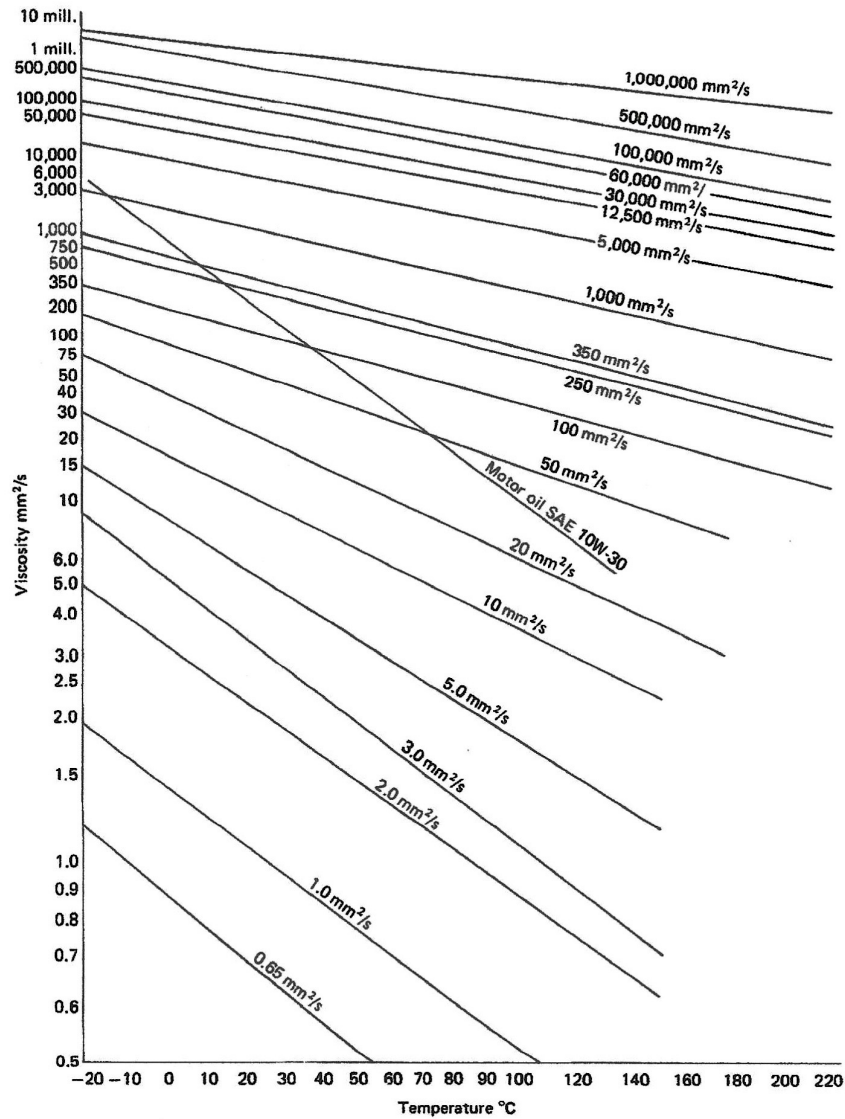


Another reaction is direct synthesis using silicon and chlorobenzene or the substitution of SiH-containing silanes with chlorobenzene, including consecutive hydrolysis reaction of the resultant phenylchlorosilanes (Figure 13).

Another is the hydrosilylation reaction, which is the addition of mostly ω -terminated olefinic molecules to the SiH unit usually by means of noble metal catalysis (Figure 14).

Finally, we have the transesterification of alkoxysilyl groups by siloxanes containing silanol endgroups or the insertion reaction of cyclic siloxanes into an alkoxysilyl group (Figure 15).

Figure 16 Viscosity/temperature correlation of silicone fluids



PROPERTIES OF SILICONE FLUIDS

The useful properties of the difunctional siloxanes and especially the polydimethylsiloxanes are a direct result of their linear structure, and are outlined here.

There is no other product type with polymers of such high molecular weight still having a liquid consistency. This results in a particularly low dependence of viscosity on temperature, and gives the silicone fluids an industrially useful viscosity-temperature characteristic (Figure 16).

Due to their semi-inorganic structure silicones fluids are much more stable against thermal and oxidative degradation than organic fluids. An additional advantage is that they scarcely absorb UV- and X-rays.

Since the silicone fluids in the low viscosity range already show considerable molecular weights, one can see that silicone fluids (other than the lowest molecular homologues) have very low vapour pressure, low volatility and, combined with their thermal stability, show extremely high flash and ignition points.

Another important characteristic based on the linear structure of the macromolecules is the low surface tension of the polydimethylsiloxanes,

Table 1 Comparison of the different properties of siloxane fluids and standard silicone fluids

<i>Product types</i>	<i>Difference from the PMDS</i>
Methylhydrogen-polysiloxanes	— increased reactivity of the SiH groups (with H-active and olefinic systems)
Phenylmethyl-polysiloxanes	— better low temperature characteristics — increased thermo-stability — weaker viscosity/temperature behaviour
Modified siloxanes	— higher affinity to polar substrates; thus in many cases poorer migration behaviour and consequently increased lubricating and releasing effect — increased reactivity corresponding to the relative functionality — repaintable
Glycolfunctional siloxanes	— partially soluble in water — surfactant behaviour in aqueous systems — poorer thermostability — poor viscosity/temperature behaviour

and thus the excellent wetting properties of these products, especially on inorganic substrates.

As well as the above-mentioned main characteristics based on the linear structure, it is important to mention that the '*m*-blocked' poly-methylsiloxanes are chemically inert. This results in some useful properties. Thus, due to the non-polar, non-reactive and semi-inorganic structure of silicone fluids a relatively high incompatibility with chemicals results which is a decisive fact for their application as release agents and lubricants.

This property, combined with the silicone fluids' insolubility in water, results in an outstanding inertness under physiological conditions. Due to their structure, the silicone fluids exhibit good dielectric properties such as high specific resistance and a high resistivity value, of about 14 kV/mm.

The properties listed in Table 1 point out the main differences between the modified silicones and the standard polydimethylsilicone fluids.

PRODUCT FORMULATIONS OF SILICONE FLUIDS

According to the requirements, silicone fluids are used as 100% materials; in diluted form — mostly in low concentrations in halogenated hydrocarbons, aromatic compounds or high-boiling white spirit; or in emulsified form as oil-/water-emulsions — mostly in low concentrations.

The silicone producers usually deliver the fluids in the following concentrations: from 10 to 50% active ingredient in solutions; and from 20 to 60% active ingredient in emulsions.

In many cases by an appropriate combination of solid siliceous material and silicone fluid, not only can other applications be found, but also an increase of effectiveness can be achieved through synergistic effects, eg:

- silicone antifoaming agents (in pure or emulsified form)
- silicone pastes (also called gel greases)
- and classical silicone greases.

To complete the picture, reactive, multi-component systems should be mentioned. These products lead to crosslinked silicone rubbers on

the prevailing substrates. This effect is mainly used in the paper and textile industry.

APPLICATIONS FOR SILICONE FLUIDS

It is not easy to discuss or demonstrate 'application possibilities of silicone fluids' as in most applications these products have an auxiliary agent effect. Due to this a wide variety of applications exists. Therefore we will discuss first pure silicone fluids, their solutions and emulsions, and later the silicone compounds.

Applications for pure silicone fluids

In Table 2 the different application fields are generally described with reference to the characteristics already mentioned. One of the most important applications of silicone fluids as pure products, solutions or emulsions is their use as release agents or lubricants. These two applications differ only in the quantity applied onto the substrate.

For release agents and/or lubricants the following properties are required: good spreading and wetting; high incompatibility with moulds and moulded material; as well as high temperature resistance. Here silicone products prove to be appropriate as release agents in elastomer and thermoplastic moulding, as antiblock agents for film, and as lubricants in the plastic industry (especially in the product combinations plastic/glass and plastic/metal), as well as in the textile industry as lubricants for polyester and polyamide fibres.

Silicones are being increasingly used by the automobile industry for anti-squeal (ie avoiding friction noise) finishes and as lubricants for thermoplastic moulded articles.

The excellent viscosity-temperature characteristics as well as the wide processing range from -50°C to $+250^{\circ}\text{C}$ allow the silicones to be used in machine construction, eg as visco-liquids in dampers and clutches, as damping mediums in the aeronautical industry, in compasses and as hydraulic liquid in brakes and shock absorbers.

Not long ago the excellent dielectric properties – combined with the characteristic high flash point and inertness under physiological conditions opened up the possibility of substituting silicones for toxico-

Table 2 Application potential of pure silicone fluids, solutions and emulsions

<i>Used as</i>	<i>Properties</i>	<i>Applications</i>
Release agents	Temperature resistant, leaving no residue in moulds, one thin coat is sufficient for many releases; prevent thermoplastic material from sticking to the processing equipment.	Release of rubber and plastic parts, for instance in the tyre manufacturing industry, in the production of moulded parts made from polyamides, cellulose acetate, polystyrene, PVC; packaging industry.
Lubricants	Impart excellent slip properties to plastics and rubber, making them water repellent at the same time; reduce surface friction.	Plastic bearings, sheeting, cutting tools, moulded and extruded parts, sewing threads.
Damping media	Retain their physical properties almost unchanged in a temperature range of over 200°C.	Speed regulators, fluid clutches (eg for fans), nautical and aeronautical instruments, gyrostatic compasses, liquid springs, recorders, time regulators, spring valves, overload relays, sound pickups.
Hydraulic fluids	Excellent viscosity-temperature performance, high compressibility and stability under shear.	Shock absorbers, pumps, recoil brake cylinders.
Liquid dielectrics	The electrical properties remain almost unchanged at high and low temperatures as well as in a wide frequency range; resistant to radiation.	Cooling agents (eg for magnetrons or other heat radiating components), transformers, condensers, high voltage tubes, spacecraft (in high altitudes air is not sufficient as cooling agent).
Water repellents	Low surface tension, highly water repellent, no nutrient medium for bacteria and fungi.	Glass, ceramic, laminates; switches, insulators; textiles.
Antifoam agents	Effective in very small amounts, odourless and tasteless.	Prevent foam formation in non-aqueous systems, eg mineral or vegetable oils.
For cosmetic and dermatological formulations	Non-toxic, form a water repellent film which allows the skin to breathe and does not irritate it.	Skin protecting ointments, sun creams, hair conditioners, insecticides.
Additives in polishes	Gloss retaining, water repellent, smoothing.	Car and furniture polishes, leather and floor polishes, fur dressing.

logically and ecologically problematic types of chemicals, such as polychlorinated biphenyls, widely used in transformers.

The possibility of using silicone fluids as waterproofing agents was probably one of the first commercially exploited applications of silicone products. This results from the marked incompatibility with water as well as the ability to achieve a high affinity to natural fibres like cotton and wool. This effect is due to the stereochemistry of the siloxane chains whereby methyl groups are orientated so as to repel water.

The property of water repellence is not only used in the textile industry but also in the cosmetics and pharmaceutical industry, eg in skin care creams, and in the treatment of glass and ampoules.

Similar properties are useful in polishes. By the correct choice of silicone fluid component the water repellency, polishing-out and detergent resistance can be dramatically increased.

Applications for silicone compounds

Antifoaming agents are considered to be the most commercially versatile application of silicone compounds, ie of silicone-siliceous-solid systems.

Pure silicone fluids are successfully used in oilfields and the oil refining industry. This results from their limited compatibility with crude oil systems, and means that despite their insolubility they are relatively easily dispersed. On the other hand aqueous systems, which often contain surfactants, require specifically compounded silicone-solid formulations containing silicic acids, such as precipitated, or fumed, silica.

The complicated physical-chemical correlations between foam stabilisation of surfactant-containing aqueous solutions and successful foam destabilisation by means of silicone-solid systems continue to be a subject of discussion in scientific publications. The main reasons why silicone antifoaming agents are almost exclusively used are their:

- insolubility in foaming systems
- high dispersibility — of pure as well as of the pre-emulsified anti-foaming agent

- low surface tension
- high surface orientation.

Examples of the main applications of silicone antifoaming agents include their use in textile dyeing and reviving systems, in cutting and drilling oils as well as in fertiliser production and application.

When discussing the application possibilities of silicone greases and silicone pastes it is necessary to be careful regarding terminology. Thus a silicone *paste* is a compound produced by dispersing an inorganic filler in the silicone fluid. A silicone *grease* is a product produced by swelling of metal soaps in the silicone fluid.

Silicone pastes find application when the liquid consistency of the silicone fluid is not appropriate, ie when a solid rather than a free-flowing product is required.

As examples of the applications one can mention the electro-insulating pastes for coating insulators, as well as the thermal-conductive pastes which are used in the assembling of electronic parts like diodes and transistors.

Silicone greases are used as sealants and lubricants. The high-vacuum silicone greases are the best known sealants for laboratory apparatus. Their good ageing stability, favourable viscosity-temperature characteristics and excellent low temperature behaviour ensure their useful role as lubricants. These greases are mainly used as lubricants with substrate

Table 3 Rank of lubricant fluid types by property for use in greases

Maximum high temperature utility – Silicone > polyphenyl ethers > perfluoroalkylpolyethers > neopentyl > esters > alpha-olefin polymers > dicarboxylic acid esters.

Low temperature fluidity – Methyl silicones > low phenyl silicones > esters > high phenyl silicones > neopentyl esters > alpha-olefin polymers > perfluoroalkylpolyethers > polyphenyl ethers.

Lubrication ability – Esters (mono, di, tri and tetra) > alpha-olefin polymers > perfluoroalkylpolyethers > polyphenyl ethers > silicones.

Radiation resistance – Polyphenyl ethers > high phenyl silicones > esters.

Cost – Perfluoroalkylpolyethers > polyphenyl ethers > silicones > alpha-olefin polymers > esters.

(From F. A. Buehler *et al*, *NLGI Spokesman*, 28, Oct. 1964.)

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combinations such as metal/rubber or in low-load bearings, especially in ball bearings.

In high-load applications the use of silicone fluids is not recommended, due in part to the low lubricating effect of silicone fluids in metal-metal combinations, and the creep behaviour of silicone fluids towards less loaded areas in the bearing limits their use.

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