No Fear of Siloxanes

Differences between antifoams based on PDMS and OMS

Introduction
This article should give you some arguments to explain to our customers the differences between antifoams based on polydimethyl siloxanes (PDMS) and organo modified siloxanes (OMS).

We already had this discussion with the VKIS (consumer cooperation lubricants in Germany), where we noticed that the terms siloxanes and silicones were not used appropriately. To give a right nomenclature of silicone chemistry and to characterise the potential danger of different silicone antifoams used in the lubricant industry we have prepared the following paper. Due to the reason that also in other industries the differences between OMS and PDMS are not well known and that we all have to argue the right way at the market, the following might be beneficial to you generally.

Antifoams based on PDMS and OMS
The group of silicones could be divided into two major groups:
- Polydimethylsiloxanes (PDMS); also known as silicone oils
- Organo modified siloxanes (OMS)

Polydimethylsiloxanes are characterised by the fact that beside oxygen atoms only methyl groups are bonded at the silicon atom (Fig. 1). Silicone oils are commonly used in conventional silicone antifoams as active components. Due to their very low surface tension Polydimethylsiloxanes are excellent antifoams, if only antifoam efficiency is required. In most critical applications they can not be used due to their high incompatibility and the tendency to create defects (for example if paintability is required).

Fig. 1: Example for a Polydimethylsiloxane
Not even through blending of the pure PDMS with other organic substances like Polyether the silicone oil characteristics could be overcome, so that the defects and incompatibility could not be avoided in that cases.

OMS – Antifoams are also based on a polylsiloxane backbone. This guarantees the low surface tension, which is needed for efficient antifoams. Nevertheless, most of the physical and physico–chemical properties are imprinted by organic side chains (e. c. copolymers of ethylene–/propyleneoxide), which are chemically bonded to the polysiloxane backbone (Fig. 2). With a suitable selection of organic substitutes it becomes possible to create organo modified siloxanes, which act totally different to silicone oils. Exemplary the excellent compatibility in aqueous media should be mentioned.

Fig. 2: Example for an organo modified siloxane
As rest R a big number of different organic substances are available. They could differ depending on the requirements of the products. Widely used are the following modifying groups:

- Polyether groups (Ethylene-/Propyleneoxide-Copolymers)
- Long chain alkyl groups
- Aryl groups
- Others (ionic or reactive groups)

As raw materials for defoamer formulations polyether modified siloxanes are used in particular.

The principle of organomodifying technology is based on the fact, that the organic part of the molecule will be increased in comparison to pure Polydimethylsiloxanes. Therefore a higher compatibility in most processes can be found. This compatibility increases internally in the modifying line Aryl – Alkyl (long chain) – Polyether. For that reason products based on OMS technology are used e. c. as additives for paints and inks, where the use of silicone oils is strictly forbidden. A negative impact of these substances on the paintability is excluded, if proper handling is guaranteed.

If we have a look on other treatments of the metal surfaces, like gas nitridation or gas carbonization, which follow the production process of metal pieces, the following is important: Due to high temperatures during gas nitridation (550 – 580 °C) and gas carbonization (950 – 1000 °C) all siloxane based products will deteriorate to SiO₂. The residues may negatively influence the building of the iron nitride layer or could build a diffusion barrier during carbonization.

To avoid these effects totally the potential washability of silicone based products is of essential importance. Also in that regard Polydimethylsiloxanes behave totally different in comparison to organo modified siloxanes. Due to their simultaneous hydrophobic and lipophobic character it is assumed that Polydimethylsiloxanes can not be removed totally with traditional detergents and cleaning methods, which are used in the metal and automotive industry. The presence of smallest quantities of these substances can lead to the a.m. problems.

Due to their more organic character and their higher polarity, organo modified siloxanes can be removed much easier and without residues with traditional detergents and cleaning methods (depending on type and degree of modification also with pure water) from metal surfaces. Therefore the a.m. problems are not expected.

By the use of ²⁹Si-NMR Spectroscopy organo-modified siloxanes can be distinguished analytically from polydimethylsiloxanes.

**Conclusion**

As a resume we can say that the term "silicone free", which is often used in the metal working industry is confusing, because in this case a total absence of Si – containing products in the metal working industry would be required. From the hitherto existing experience this is not necessary, because organo modified siloxanes do not lead to problems in the metal working industry, presupposed these products are handled in a proper way. From our customers we never heard about negative points in that regard. Therefore the term "silicone free" must be substituted by the term "silicone oil free" or "polydimethyl-siloxane free".