

The Myth of Silicone Ban in the Automotive Industry

The use of silicones in automotive applications opens great opportunities. However, there are also certain risks, especially in e-mobility applications, so that in the supplier industry there is sometimes the myth of a silicone ban present. As part of a bilateral project, Audi and Fraunhofer IFAM have now investigated the outgassing behaviour of silicone-containing materials in the environment of mechatronic and electronic components in more detail.

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The risk posed by the use of silicones has been known for a long time. It has been handled by the targeted selection of materials or by banning silicone-containing materials and auxiliary materials in certain production areas. For example, coatings, paints, sealants, insulating materials, lubricants, potting compounds, release agents, insulation or heat conducting materials have been identified as potential sources of silicone. The silicone-based polymer systems [1] used in the automotive industry are summarized in the Info Box. The development trend towards autonomous driving with its power electronics and e-mobility with its high-voltage assemblies all strongly depend on active

thermal management and the targeted use of temperature-stable silicone rubbers. For example, silicone-based thermal interface materials (TIM) are often used in large quantities as so-called gap fillers to ensure robust thermal management. Another example is the electric drive train including the high-voltage battery, which is located in the vehicle exterior. Here, all affected components must be protected from water penetration with the help of high-temperature-resistant seals, and silicone is often used for this purpose. Silicone is also used for insulation materials to ensure the high-voltage safety of all assemblies. However, the use of silicone also results in risks for mechatronic systems, as the con-

tamination of electrical contact surfaces with volatile and oily siloxanes can result in high-resistance electrical contacts. This behaviour requires special attention in the context of e-mobility, as it is extremely critical for electronic and mechatronic applications, such as e-machines with their auxiliary units (DC motors), mechanical switches and relays, power electronics, high-voltage components, contactors in batteries and similar components. The damage is essentially related to the amount of volatile silicone components and their wetting properties. Due to low surface energies of approx. 20mN/m, Siloxane tend to stick to almost all surfaces. Among other things, this leads to wetting disorders. This is the main reason why extensive silicone bans have been imposed in painting or bonding processes. Ceramic sensors or optically active surfaces, for example in headlights and cameras, can also be affected.

However, in the field of mechatronic components, a ban on silicone-based materials for the applications described above is not expedient, as the good thermal and low-temperature flexible properties of silicone rubbers for electronics are essential to comply with latest automotive re-

Silicone Materials in (E-)Vehicles

Silicones are used in multiple reaction systems in the automotive industry. Single-component RTV systems (moisture-curing – usually neutrally curing in the vicinity of electronics) and two-component, addition-curing systems (Pt-catalysed) are of the greatest importance. The latter, as in the case of a potting compound, are crosslinked directly after application or are already used as LSR (Liquid Silicon Rubber) or HTV (High Temperature Vulcanization) as crosslinked rubbers, e.g. for single wire seals in connectors [1]. However, solvent-based systems are also used, e.g. for antifogging coatings.

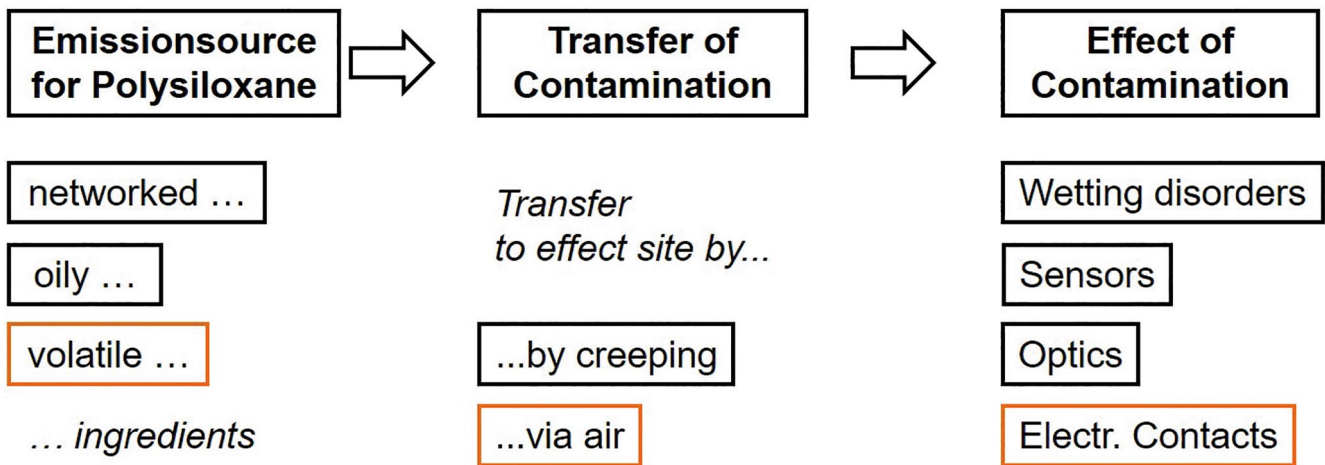


Figure 1 > Interrelationships of the effects of silicones – the points considered in the project are outlined in red.

quirements. The trend towards higher operating and ambient temperatures or increased specific power losses and generally harsher ambient conditions reinforces this effect, especially in the field of e-mobility with its enormously high-power densities.

Motivation and project goals

Although the basic risks and error mechanisms were known, in the recent past anomalies occurred in the development of mechatronic components at Audi that were attributed to silicone contamination. In the process, it became apparent that there were no sufficient specification requirements or test regulations for determining and evaluating silicone-related risks for mechatronic components within the Volkswagen Group. Therefore, as part of a bilateral collaboration between Audi and the Fraunhofer Institute for Manufacturing Technology and Applied Materials Research (IFAM), basic principles for the evaluation of silicone emissions in automotive applications were developed. The overall objective was to comprehensively assess and prevent risks associated with the use of silicone materials in encapsulated electronic and mechatronic assemblies. As shown in *Figure 1*, the project focused on the most significant contamination pathway of volatile siloxanes via the gas phase.

As a first step and basis for all further investigations, measurement procedures, which have meanwhile been released as test specifications PV3040 and PV3055 in the Volkswagen Group, were developed

for the validated determination of silicone emission and silicone contents. In a second project step, the focus was on the effect of silicone contamination and the question of the concentration level where no effect on the respective applications will occur (no-effect level). The results of this part of the project are to be published in the near future.

Practical examples from component development

For the electrification of vehicles, mechatronic/electronic assemblies are basi-

cally indispensable. Two examples of silicone contamination are described below.

• **DC brushed motors in actuators and kinematic drives**

Electromechanical auxiliary units, like brush motors, so-called small drives, are operated both in the combustion drive and in the e-drive (*Figure 2*). Typically, these are installed in the vehicle exterior, which makes it necessary to seal the assemblies under additional high temperature loads. Due to their good temperature resistance, sealing materials made of silicone are almost exclusively used here. If

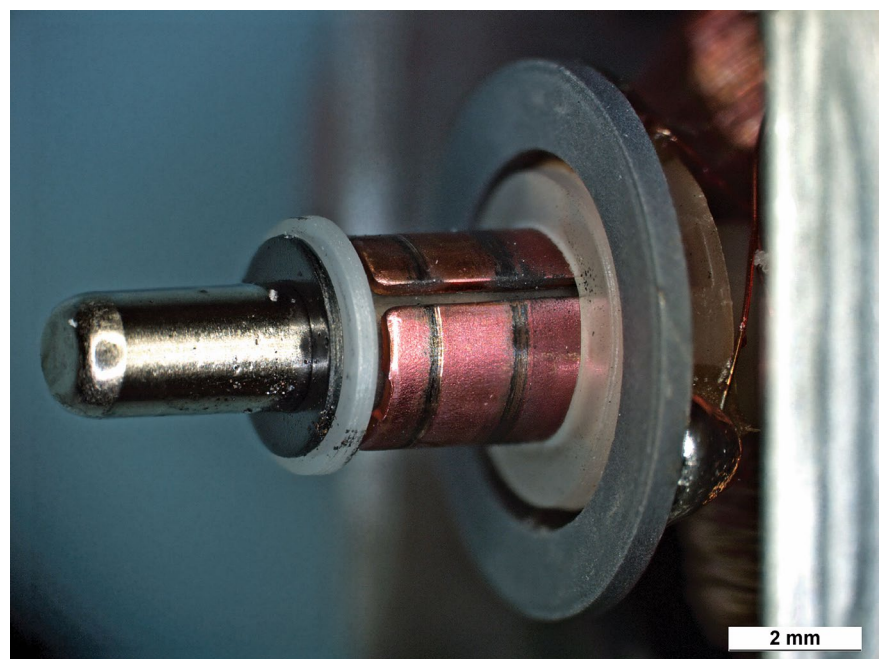


Figure 2 > Failure of a DC motor due to silicone outgassing from the seal

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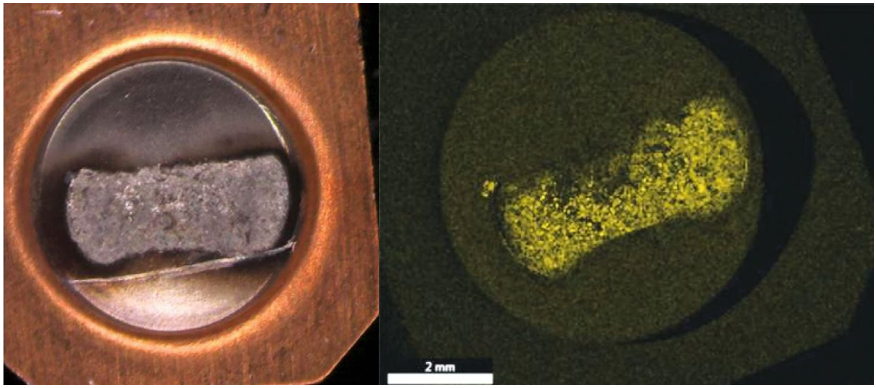


Figure 3 > Comparison of microscopy and EDX mapping (Si) of an electrical relay contact that failed due to emissions from the plug seal

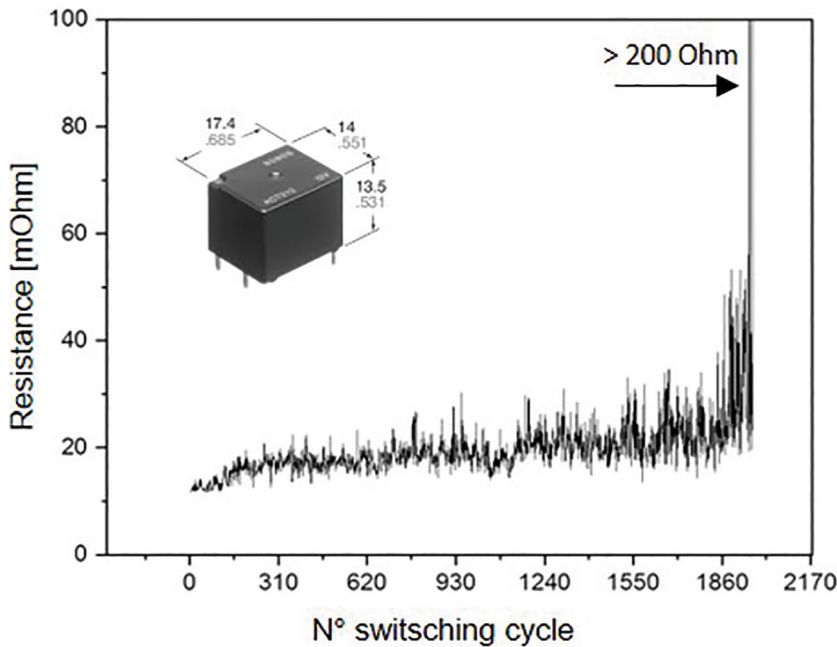


Figure 4 > Spontaneous increase in resistance of a pre-opened twin type relay after 1966 switching cycles during operation in a defined silicone gas atmosphere (ACT 212, Panasonic, 12 V /10 A)

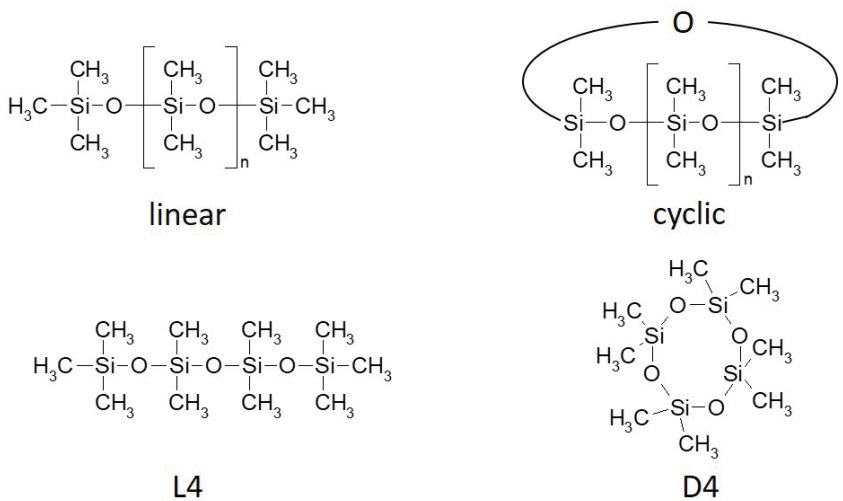


Figure 5 > General structures of cyclic and linear siloxanes and respective examples of chain length 4

the silicone materials chosen for the application exhibit excessive outgassing behaviour, volatile siloxanes can occupy the contact surfaces of the rotor or commutator. Under Operation of the motor, a so-called brush fire (breakaway spark or short circuit) occurs. In this plasma-like arc, the siloxanes are converted so that an electrically non-conductive silicon dioxide (SiO₂) layer is formed on the contact surface. This process is also called vitrification. The contact thus becomes highly resistive and the motor no longer starts, i.e. it fails to function.

● **Electromechanical switches, relays and contactors**

Despite the use of semiconductors, relays and contactors are experiencing a renaissance with e-mobility, as high currents and voltages must be switched in the safety concepts of HV assemblies. Depending on the electrical concept, a switching spark occurs when the switch opens or closes, which, as already described above, results in a silicone-contaminated contact surface which becomes highly resistive by conversion of the siloxanes into silicon dioxide (Figure 3). For the mechanism of action of volatile siloxanes on contact surfaces, it is generally hypothesized that in a first step the siloxanes from the gas phase lead to monomolecular adsorption layers on the contact surfaces and in a second step are converted from there to SiO₂ in the plasma-like state of the arc [2]. The change in resistance generally occurs spontaneously during operation at the moment when the SiO₂ layer on the contact is completely closed. Figure 4 shows an example of the spontaneously increasing electrical resistance of a relay operated in a siloxane gas atmosphere.

In the examples mentioned here, the silicone source was not always installed directly in the component. In the case of the relay failure, for example, the silicone source was a single-wire seal from a connector of a neighbour component, which was gas-tight connected via the cable sheathing. In summary, three categories of silicone-containing sources could be defined:

1. Silicones present in the assembly itself, e.g. seals, potting, lacquers, adhesives, lubricants, etc.
2. Silicones present in adjacent components or at the installation site, e.g. wiring harness, trim parts, etc.

3. Silicones introduced by the customer, e.g. cosmetics, cleaning and care products, etc.

Only the sources for points 1 and 2 can be evaluated and taken into account during development by the OEM. The third case is not under the direct influence of the OEM, but must be classified as 'foreseeable misuse' and also taken into account in the development.

Emission of volatile siloxanes

Most technical silicones are based on polydimethylpolysiloxanes (PMDS), i.e. there are two methyl side groups on the silicon atom. *Figure 5* shows the essential structural features of volatile siloxanes and an example based on the chain length 4 (corresponds to 4 silicon atoms). The cyclic species of ring size D3 to D9 (D stands for dimethylcyclosiloxane) are of great importance in terms of occurrence and evaporation. Linear L-species (L for linear) can also be detected more rarely or in significantly smaller quantities. In addition, branched or other silicon-containing accompanying substances from the synthesis can occasionally occur. The vapour pressures decrease with the chain length of the species accordingly, with D and L species of the same chain length showing almost identical volatility. Thus, the vapour pressures along the homologous series D4 / D5 / D6 decrease from 140 to 33 and 4.6 Pa (at 20 °C) [3]. Species with chain lengths of 10 and greater exhibit such low volatility at typical maximum application temperatures of up to 200 °C that they cannot be detected in the gas phase anymore. *Figure 6* displays a schematic mass spectrum of a linear silicone. It can be seen that the volatile siloxanes (VS) are not low-molecular monomers or oligomers at the lower edge of the molar mass distribution, but rather non-reactive by-products that already originate from the synthesis of the silicone raw materials and whose concentration/volatility is not affected by the curing reaction. It follows directly from this that the network density or chain length does not give any indication of the content of volatile siloxanes, so that silicone gels or even oils, for example, can also have low emissions. Volatile siloxanes cannot be completely avoided in the today's synthesis route and are separated at great expense by fractional distillation when used with the highest requirements, such as for aerospace applications.

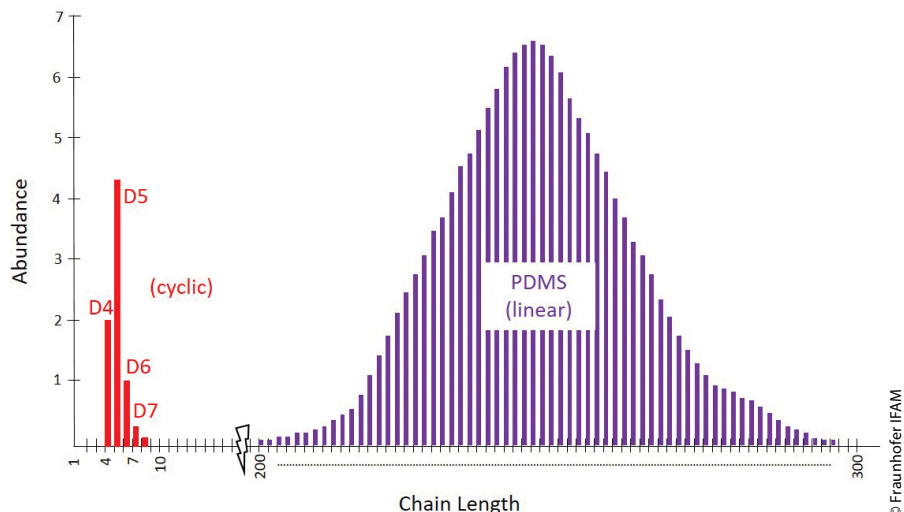


Figure 6 > Principle sketch of a mass spectrum of a linear polydimethylsiloxane with desired product (violet) and low-molecular cyclic by-products (red)

A cross-linked silicone usually contains 3 to 20 % of non-cross-linked (extractable) species, whereby this proportion can also be over 50 % in silicone gels swollen with silicone oils. Depending on the product, portions of 0.1 to 1 % can be contained as potentially volatile portions [4].

Selection of the determination method for volatile siloxanes

The basis for assessing the risk of failure is a sufficiently accurate measurement of

the volatile components described above. As shown in *Figure 7*, various analytical strategies were considered, although the surface analytical methods were not considered in detail due to the project's focus on transfer via the gas path. Thus, the questions "How much volatile siloxanes (VS) are contained in the material?" and "How much is transferred to the gas phase under the application conditions?", i.e. what concentration will occur in the gas phase, essentially have to be answered. Because of the high sensitivity and differ-

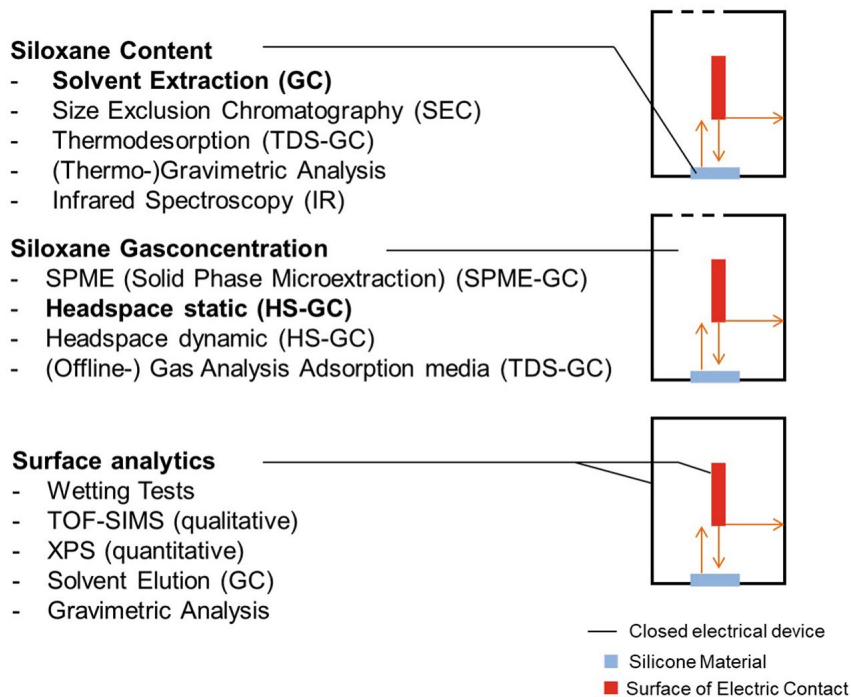


Figure 7 > Different strategies for analysis of siloxanes



Figure 8 > Sample preparation – right: extraction according to PV 3055 (1 g silicone on 10 ml heptane), left: emission according to PV 3040 under standard conditions (50 mg silicone on 20 ml gas volume)

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Figure 9 > Typical gas chromatography system with autosampler: oven (left), headspace tray (centre) and tray with vials (right) for liquid injection

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entiation of the result in individual species as well as the wide distribution, gas chromatography was chosen as the detection method.

According to the test specification PV 3055 mentioned at the beginning, the content of volatile siloxanes is determined by means of a fully exhaustive extraction of the material to be tested in heptane over 24 h at 1 g sample weight and 10 ml solvent (Figure 8 right). The solution is then injected into the gas chromatograph and the content of each species is determined quantitatively. The content is given in ppmw, where the ‘w’ stands for ‘weight’, and the unit is thus equivalent to µg/g.

For an emission value according to test specification PV 3040, sample material is

tempered in a closed vessel (Figure 8 left) and the gas concentration of volatile siloxanes is determined. This is the decisive variable for the risk of siloxane induced failure. The gas concentration depends on the amount of silicone material in the electronic component and the air volume of the component or its quotient (the load). In addition, the temperature is important, whereby T_{max} of the value defined in the specifications can be used here as a worst-case scenario in each case. In order to determine the concentration of volatile siloxanes identical to the application for the electronic component, an experiment is carried out in which the load (amount of silicone per gas volume) and temperature are adapted from the en-

capsulated electronic component. To enable comparison of the emission behaviour of different materials at an early stage of development, 145 °C at a loading of 2.5 mg/ml was set as the standard analysis conditions. The result is given in ppmv, where the ‘v’ stands for ‘volume’, and the unit is thus equivalent to µl/l.

The procedure, including temporal temperature control and gas sampling, can be fully automated on common gas chromatographs (Figure 9) using autosamplers. Therefore, large sample contingents can be analysed in a short time. Figure 10 shows a typical result of an emission analysis. In the chromatogram shown, mainly D species are visible with a decreasing tendency towards higher homologues corresponding to the vapour pressures. In addition, in this case trimethylsilanol could be detected as a species, which can sometimes occur in considerable quantities in the raw material as a by-product.

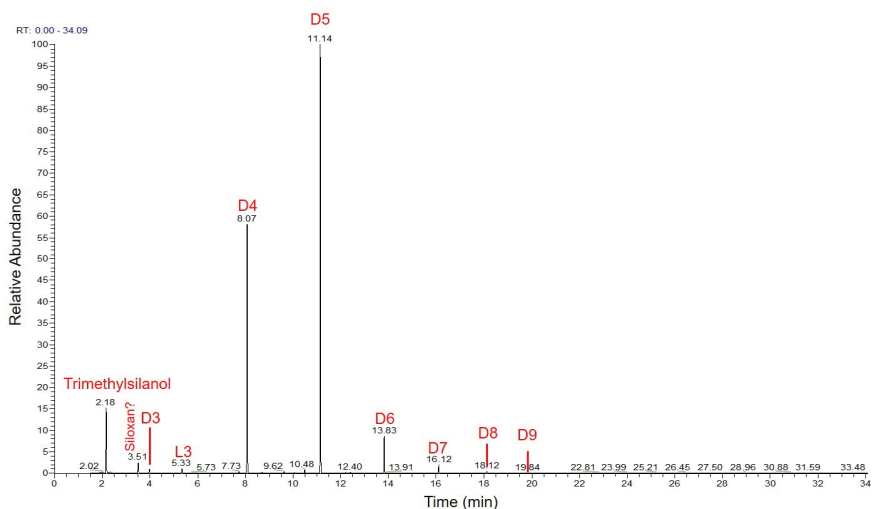


Figure 10 > Typical chromatogram of an emission analysis at 145 °C with high D- and low L-fractions

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Round robin tests

To further establish the methods, inter-laboratory tests were carried out on three representative silicone materials. In addition to the internal laboratories of Volkswagen and Audi, the Fraunhofer IFAM laboratory and the Wacker Chemie laboratory were also recruited as project participants. A detailed exchange of experience took place about analytical procedures, device parameters and a comparison of results. This resulted in measurement deviations of ≤ 10 % for the content determination and ≤ 20 % for the emission de-

	PV 3055 (Content)	PV 3040 (Emission)	
		Procedure A (standard)	Procedure B (electronic device)
Sample preparation	Solvent extraction: 10 ml heptan to 1g silicon, 24 h / RT	Weighing: 2,5 mg sample per ml volume of headspace glas	Weighing according to load of mg silicone in ml volume of housing
Measurement	Injection of aliquots in gas chromatograph (GC)	Tempering 145 °C / 1 h (primary emission) and 10 h (secondary emission), injection aliquot of gas compartment in gas chromatograph	Tempering at T _{max} 1 or 2 h (primary emission) and 10 h (secondary emission), injection of aliquot of gas compartment in gas chromatograph
Quantitative Analysis with Flame Ionisation Detector (FID)			
Calibration	External calibration with D5	External calibration using D5-doped headspace glasses	
Result	Content of volatile siloxanes in retention area of D3 to D9 in ppmw (µg/g)	Gas concentration of volatile siloxanes in ppmv (µl/l) using standard conditions and possible presence of secondary emission	Proposed gas concentration of volatile siloxanes in ppmv (µl/l) at user conditions and possible presence of secondary emission at T _{max}

Table 1 > Summary of the new test specifications (PV)

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terminations. The results were directly used for test specifications PV 3055 and PV 3040. Thus, a valid procedure for material characterisation and prediction of the damage-relevant gas concentration in the closed electronic component is now available (Table 1).

Material screening

Prior to the round robin test, the emissions and contents were determined in a screening of 18 silicone materials in use at Audi. The sum values of all volatile siloxanes in the retention time range D3 to D9 are listed in Figure 11. Values between 5 and 5,000 ppmw were determined for the volatile siloxane content (blue bars in Figure 11).

For the emissions (red squares in Figure 11), gas concentrations of 1 to 400 ppmv were found. A comparative value is not yet available here. In the literature, values of 1 to 30 ppmv are discussed, above which an effect on electromechanical components occurs [5]. As already mentioned, the evaluation of such a 'no-effect level' is the subject of a further publication. When comparing the emission and content values, it is noticeable that high contents do hardly correlate to high emission values. This unexpected effect can be attributed on the one hand to the fact that the concentration profiles of the contained species D3 to D9 are different for the materials under investigation. For example, samples with the same VS content emit less when high proportion of D9 is present than materials with the same high content of very volatile D3 due to the low vapour pressure. On the other hand, the in-

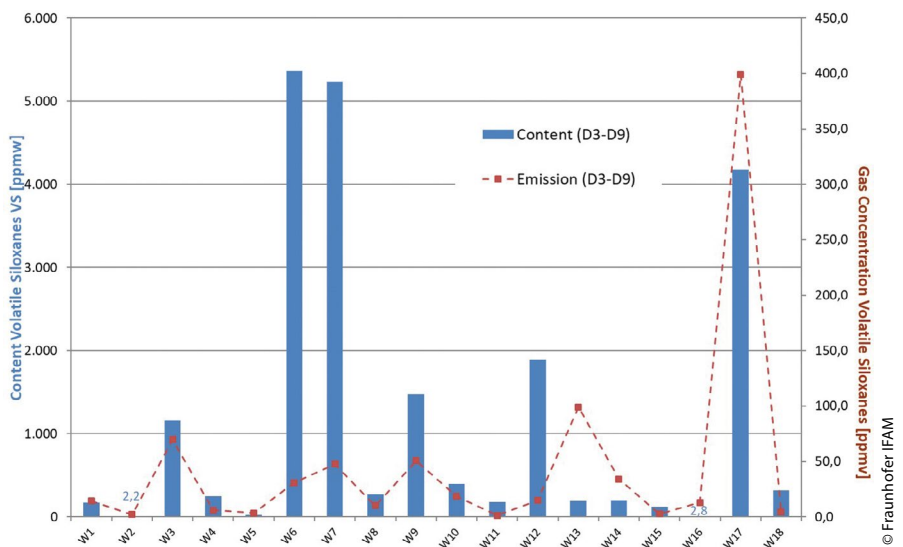


Figure 11 > Results of the volatile siloxane-content and -emission determinations (145 °C) on 18 silicone materials

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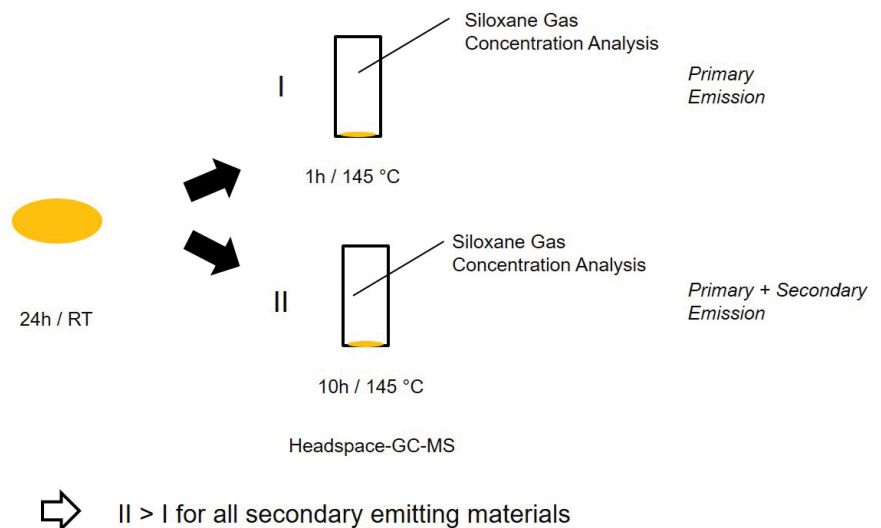


Figure 12 > Schematic testing procedure for secondary emission

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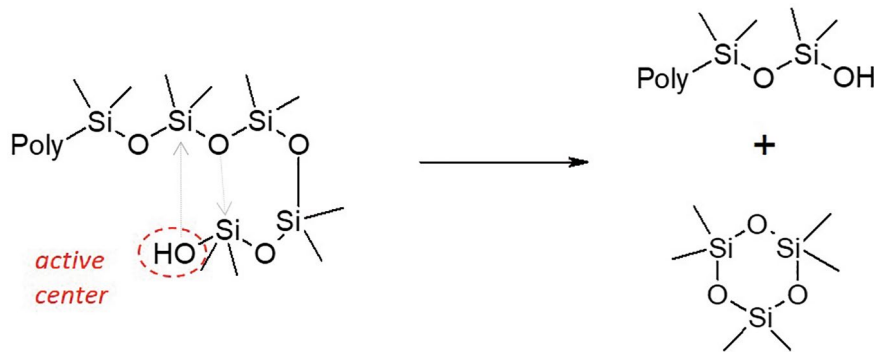


Figure 13 > Backbiting process to replicate volatile siloxanes [7]

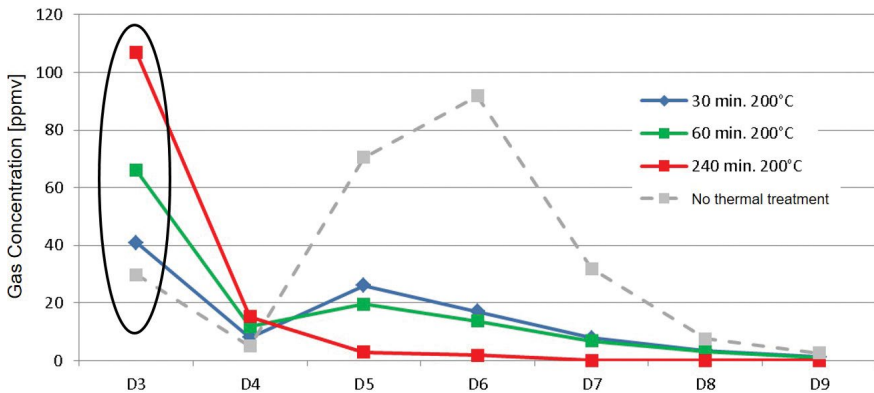


Figure 14 > Results of the gas concentration profiles of a secondary emitting silicone rubber – before and after tempering at different times at 200 °C

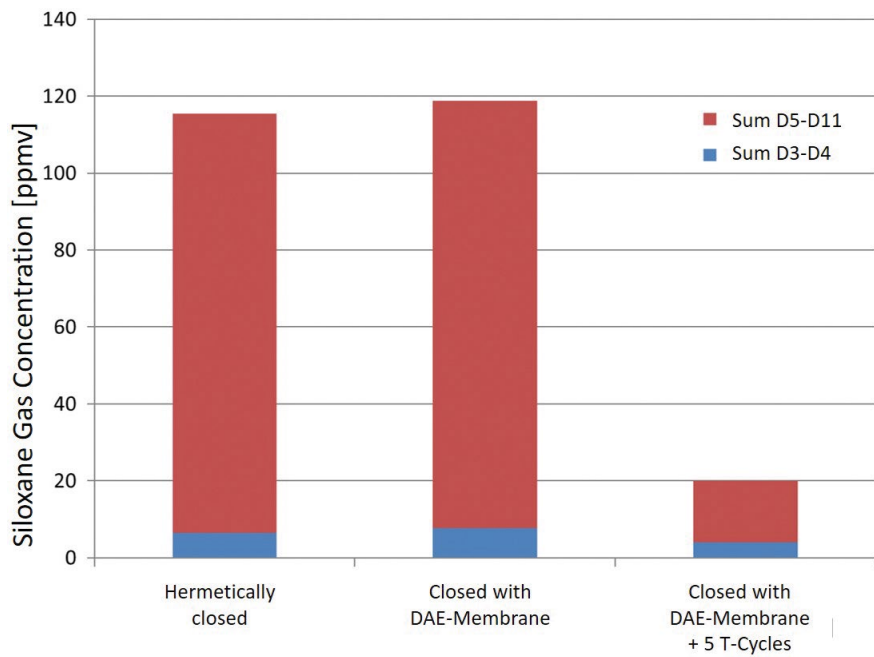


Figure 15 > Gas concentration within a closed compartment, closed with DAE and with DAE after climate change (from left to right)

teraction possibilities with the surrounding matrix also seem to have a significant influence on the vapour pressure and thus the resulting gas concentration. These ef-

fects are described in physical chemistry via Henry coefficients, which, however, are not available for the matrices investigated.

Secondary emission

Within the project, some samples showed increased concentrations, especially of D3 and D4, after tempering the samples. A replication of volatile siloxanes during tempering, a so-called secondary emission, was detected. Since this can contribute considerably to the emission of volatile siloxanes, an additional emission test with prolonged tempering was added to the test scheme of PV3040 (Figure 12). If the emission value after extended tempering is significantly higher than the one after short tempering, the material must be classified as a secondary emitter. The reason for the reproduction of volatile siloxanes lies in the thermal degradation reaction known for silicones, which occurs in particular at terminal OH groups of the siloxane chains and is referred to as 'backbiting' (Figure 13) [6].

In the screening study, 6 of the 18 examined silicone materials were identified as secondary emitters, with an increase > factor 10 occurring in two cases after tempering for 24 h at 145 °C. This phenomenon, which was previously little noted, is of importance for applications for mainly two reasons. On the one hand, after placing the silicone in a closed compartment and operating the component at increased temperatures, significantly higher gas concentrations are to be expected than can be predicted on the basis of the initial contents. Secondly, the practice of tempering silicone rubbers to reduce the proportion of volatile siloxanes needs to be critically discussed. As can be seen in Figure 14, in a secondary emitting material, a tempering process expels more of the long chain volatile siloxane species – however, volatile D3 is also reproduced and is detected in higher concentrations in the gas phase upon tempering. For such materials, a consideration must be made, or the tempering process must be adapted to the material behaviour.

Influence of pressure compensation membranes

A legitimate question was the influence of pressure compensation membranes (DAE) on the concentration in the interior, which are often used for closed components. These are primarily PTFE membranes that are stretched to create a defined micro-perforation. To evaluate the influence, silicone materials were stored

in tightly sealed jars and the concentration of volatile siloxanes was determined. The results were compared with experiments in which the jars were sealed with a DAE. Figure 15 shows the values measured for the gas concentration during storage with constant temperature (60 min at 145 °C) and after climate change. These results and also theoretical considerations on the relationship between molecule and pore size suggest that the membrane is permeable to volatile siloxanes. However, diffusive transport is negligibly slow and takes hours. Thus, an exchange with the ambient air seems to occur only when the temperature changes entail in a convective transport accordingly. It can be assumed that such concentration-reducing breathing occurs during regular operation of an electronic component due to self-heating and change of ambient temperature.

Use in practice

The results show that very large differences in content and emissions are to be expected for the silicones used by Audi. They also confirm the high relevance of a detailed material evaluation in the early development phase in order to significantly avoid the risk of failure. The Volkswagen Group ensures that all known component-relevant requirements and test specifications are available to every developer by means of group-wide coordinated and approved specification templates for electronics. Since not all requirements are relevant for every component, the influences and effects of the damage mechanisms of volatile siloxanes on electronic/mechatronic assemblies are described in the chapter on silicone-containing materials. The specification writer decides on a project-by-project basis whether the requirements are necessary or not, i.e. there is no fundamental ban on silicone-containing materials. The two new test specifications have been included in the Group's specifications template for electronics and thus apply to both in-house developments and purchased parts.

For the future, a standard specification of the volatile content of silicones on the material data sheets of the material manufacturers according to PV 3055 would be desirable. Furthermore, from Audi's point of view, all suppliers of electronic/mechatronic assemblies should follow PV3040 so that a project-related risk assessment is possible. In this way, the use

of materials containing silicone in high-performance and high-voltage electronics can be assessed and the myth of a ban can also be counteracted.

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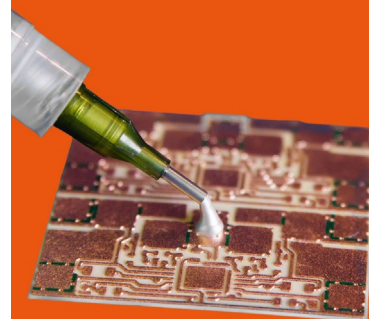
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