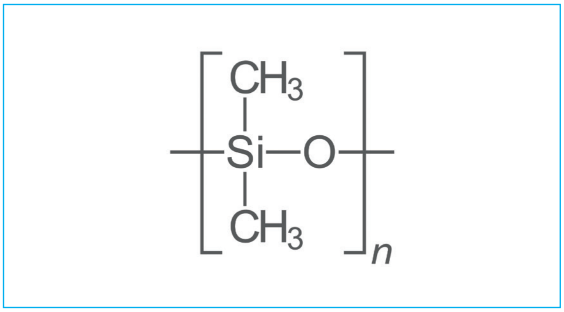

Fig. 1 Chemical structure formula of silicone oil (polydimethylsiloxanes)

Win Labuda, Christian Wendt

Silicone oil (polysiloxanes) as a contaminant

analytical determination and cleaning

Clear & Clean - Research Laboratory
September 2021 Issue

Silicone oils (polydimethylsiloxanes) are colorless, odorless, non-reactive liquids with a property profile that differs significantly from that of mineral oils. Silicone oils do not have carbon-based chain molecules but rather siloxane-based chain molecules as their basic structure [1] (Fig.1). This means they have a higher flash point, higher temperature resistance, higher stability over a wide temperature range, more pronounced hydrophobicity, lower surface tension, chemical inertness and good chemical solubility. It is understandable that such a substance has a wide range of technical uses. As is so often the case, however, the desirable properties for one application are undesirable for the other. The property of silicone oil as a good release agent also results in a reduction in the surface adhesion of paint and adhesive applications. On the other hand, the good flow and migration properties also cause electrical contacts to be gradually covered with an insulating layer, which then results in contacting problems and problems with solder joint strength. Last but not least, object surfaces coated with a silicone oil layer are difficult to clean.

Applications

Silicone oils are also widely used in industry for the production of plastic additives, textile and fiber auxiliaries, lubricants, antifoam and release agents, sealants, plasticizers and, last but not least, for hair and skin care products. The latter application has a specific consequence for the techniques of working in a cleanroom environment. If cleaning is carried out manually, there is a risk of object surfaces being contaminated with traces of silicone oil if this is not prevented by wearing suitable protective gloves.

Miscibility, solubility

Polydimethylsiloxanes are miscible with aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, ethers, esters, ketones and higher alcohols. On the other hand, they are not miscible with polar solvents such as water or short-chain alcohols such as 2-propanol.

As a contaminant

Silicone oils also have some properties that characterize them as contaminants [1]: As free substances in the proximity of metals, they pose the risk of creeping, i.e. depositing on contact surfaces, for example, where they change the electrical surface resistance there. Gubbels, et al. [1] divide the possible polysiloxane contamination into three groups: Two of them arise from the gas phase: 1- volatile silicones from preparations such as fluids and pastes and 2- volatile silicones from aerosols. In Group 3, the contaminant affects the contact and spreading of the application’s miscibility and solubility as contaminant pastes and fluids. They are also the cause of adhesion failure on painted surfaces, circuit board damage and filmic contamination in general.

Relevance

The findings described in this article mainly concern the effects of silicone oil on the *consumables for clean working techniques*, also known colloquially as cleanroom consumables. In the context described here, this includes the following consumer products:

- Cleaning wipes
- Cleaning sticks (swabs)
- Mops for cleaning floors
- Cleanroom gloves
- Cleanroom clothing

High-tech cleaning wipes

High-tech textile products such as cleaning wipes made of PET or PET / PA knitted fabrics often come into contact with chemical production by-products during yarn production. They can contain polydimethylsiloxane as component of what is known as "spinning oils". This also applies to the downstream knitting process and the „knitting oils" used.

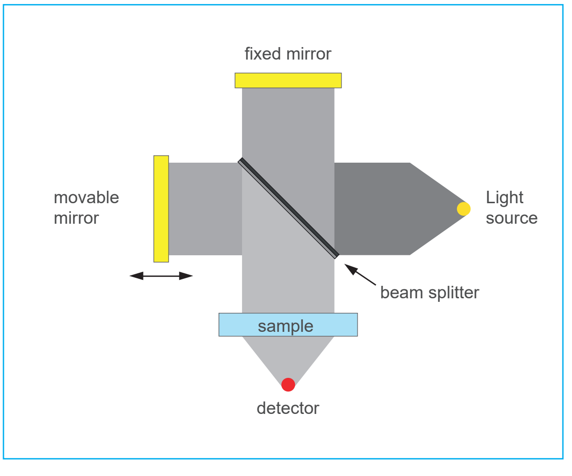

Fig. 2 Scheme of an FTIR spectrometer

When using precision cleaning wipes in their production environment or in laboratories, the occurrence of silicone oils must sometimes be excluded as far as possible. It is therefore necessary to know any residual contamination that may be present before using high-tech wiping agents or to ensure analytically their transfer probability to the critical process and object surfaces. In the experience of the authors, however, this is only possible in cooperation with an experienced cloth manufacturer. He/she should have the following analytical instruments: O2 plasma cleaning system, gas chromatograph, alternatively HPLC measuring station, FTIR spectroscope. The manufacturer must also be willing and able to freely share the knowledge gained with the wipe user if harmful contamination is actually to be ruled out.

In order to remove traces of silicone oil from critical object surfaces by wiping cleaning processes, it is important to ensure that the wiping agents used are not themselves contaminated by silicone oil. "Silicone oil-free" is to be expected from wiping agents that consist of natural substances such as cellulose and cotton-containing materials, in the manufacture of which silicone oils are not used in accordance with the process. The disadvantage of these wiping agents, however, is their lower material strength compared to the polyester cloth and thus increased particle release. If these are exclusion criteria, then decontaminated PET or PA knitted wipes remain the alternative. In our laboratory, four high-tech wipes were tested in the headspace gas chromatograph:

Polyester, not decontaminated =	contains silicone
Polyester, decontaminated =	silicone-free
Cellulose I =	silicone-free
Cellulose II =	silicone-free

Test certificates: Caution!

Users as well as distributors of cleanroom consumables rarely have the instruments and trained testers to test the material properly. An external material test and certification for products that are critical from a manufacturing point of view is therefore of interest to certain users and also distributors. Some companies / institutes serve precisely this gap in the market and offer material tests and certificates on a commercial basis. Distributors from East Asia in particular like to use the option of a product association with illustrious institutes or certificate names to elevate the image of their no-name products. It is therefore helpful to be aware of some of the problems that can arise with such issuing of certificates:

- A test and release certificate with a period of validity of more than 1 year (or even 5 years!) should always be questioned. No one can guarantee the product quality in advance for this long period of time.

- Test certificates that are only issued to the name of the distributor and his/her product identification make it more difficult for the user to contact the manufacturer in the event of a complaint. On the other hand, they allow the distributor to tacitly change the manufacturer and product of the certified products at any time and thus deliver a lower-quality product without the user noticing this or the certificate losing its validity.

- Test certificates of this kind are not infrequently used by East Asian importers for advertising purposes. For example, the distributors order a certificate from the testing institute for the most technically trivial parameter of a cleaning wipe such as „water absorption" according to DIN EN ISO 9073 - 6 and display the certificate on the Internet or in the catalog. Employees in a hurry who are not technically trained can get the impression that the wipe is fully qualified even though only the parameter „water absorption" – one of many possible parameters – is qualified.

- The above-mentioned concerns also and in particular relate to the possible contamination of the consumables with trace elements from substances that e.g. are not even known to the East Asian consumables producers because they are of no relevance for the majority of the product users there or remain undetected for a long time in the absence of their own analytical instruments.

In the case of nitrile gloves – also known colloquially as *cleanroom gloves* for use in a clean working environment – it is often the case that silicone oil residues are contained in the nitrile matrix [4]. This can be particularly problematic if such gloves touch critical object surfaces that are prepared, for example, for processes of adhesive joining (bonding). For such applications, the user is advised to obtain the gloves directly

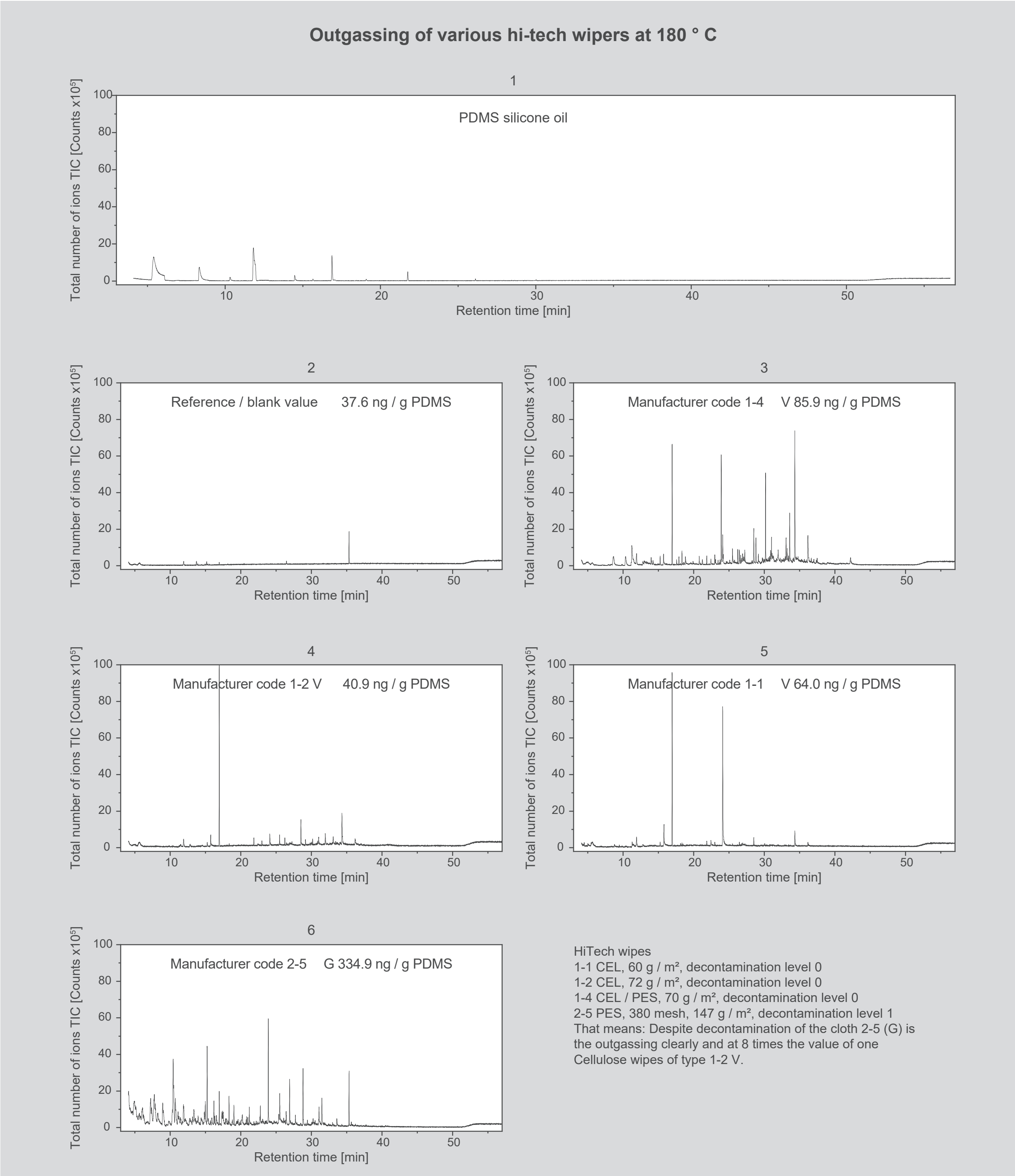

Fig. 3 Analysis of the outgassing of some coded (Tables 3 to 6) high-tech wipes from various manufacturers using Headspace GC / MS at a heating temperature of 180 ° C. Under these test conditions, silicone oils can be precisely determined using specific mass fragments. (Clear & Clean Research Laboratory)

from the manufacturer and to request a certificate from them stating the residual silicone oil contamination. If smaller quantities are required, this may encounter difficulties because the statement "silicone-free" does not normally refer to the trace area.

Traces of silicone oil can also and especially be found in cleanroom clothing. However, due to the lower likelihood of contact with endangered parts, there is less danger to operation than with the two previously mentioned products.

Analytical determinability

There are a number of technical articles that relate to the analytical determinability of silicone oils down to the trace range. However, their statements are not specifically related to the consumables used in clean technology. We therefore wanted to come to our own statements on the basis of tests with the instruments we have available. We will also go into the interesting findings of Tobias Mundry in his dissertation below.

FTIR: There are a number of technical articles that relate to the analytical determinability of silicone oils down to the trace range. However, their statements are not specifically related to the consumables used in clean technology. We therefore wanted to arrive at our own statements based on tests with the instrumentation available to us. We will also go into the interesting findings of Tobias Mundry in his dissertation quoted below.

FTIR: Our own laboratory tests were carried out to quantitatively determine any traces of silicone oil on the inner surfaces of PU fleece gloves by means of infrared spectroscopy (FTIR). The characteristic spectrum for silicone oils is shown in Fig. 4.

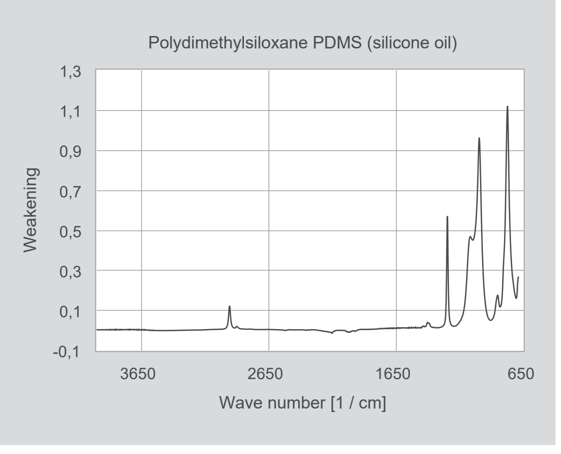

Fig. 4 FTIR spectrum of silicone oil / polydimethylsiloxane PDMS

In order to obtain plausible results, the FTIR spectrometer used for this investigation was calibrated with silicone oil masses of 50 to 1000 nanograms. The corresponding calibration function is shown in Fig. 5.

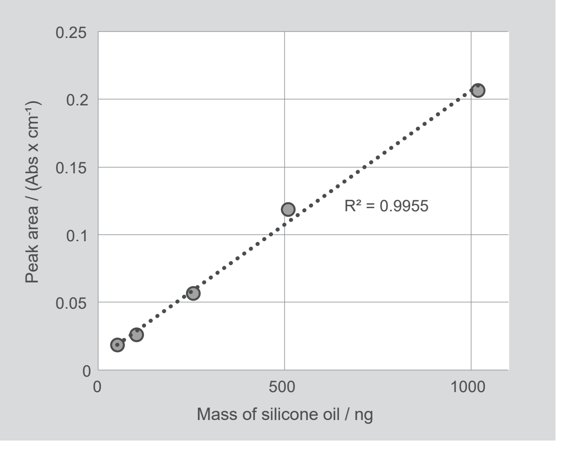

Fig. 5 Calibration function for silicone oil masses from 50 to 1000 nanograms for the FTIR spectrometer used in this investigation.

In tests with 2-propanol of 99.99% purity, there was, as expected, no evidence of silicone oil traces after 20 minutes of microwave extraction of the PU gloves in the FTIR using the ATR or dial-path method.
Manfred Hagmann [5] from SAS Hagmann wrote in the Auugst 1999 issue of his company publication under the heading *Quantitative determination of silicone oil on metal surfaces:* „Silicone oils are difficult to detect, especially in mixtures with other oils". In it he shows two FTIR spectra. The 2nd spectrum contains the section 470 - 1350 (cm-1) in an enlarged form. In this spectrum, a clear peak of 80% is visible at around 1100, which is marked with the comment "little silicone", while the same peak at 30% bears the comment "a lot of silicone". However, the author does not provide any explanatory dimensions.

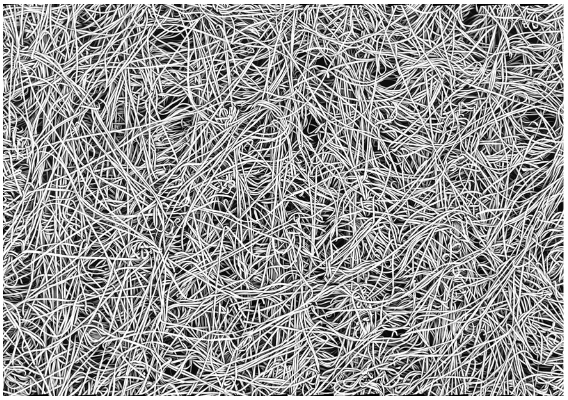

Fig. 6 Fleece surface, wipe code 1-2 V, image width 3 mm, SEM photo Yuko Labuda

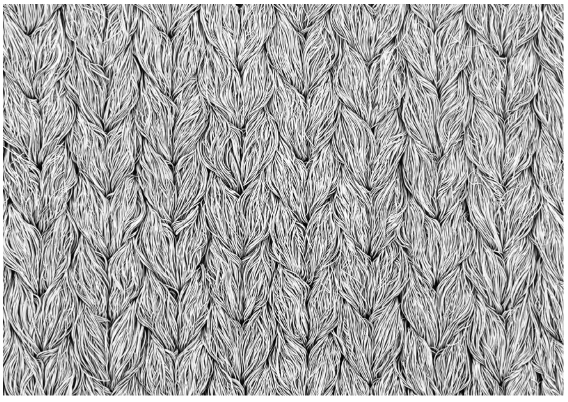

Fig. 7 Knitted fabric surface, wipe code 2-4 G, image width 3 mm, SEM photo Yuko Labuda

In his interesting dissertation, Tobias Mundry [2] writes in detail on the selection of the analytical method in the context of stoving siliconization in pharmaceutical glass packaging materials:

GC / MS: In order to determine trace levels of silicone oil on surfaces that are at risk of contamination, the ToF-SIMS time-of-flight ion mass spectrometry is a reliable, albeit very expensive, analysis method. This makes it easy to analyze the top three molecular layers of surfaces. The depth of analysis of this method is around 1 nm. Elements and molecules can be recorded at the same time. The detection sensitivity is in the low ppm range. However, quantification is only possible to a limited extent with this analysis method. In contrast, the method allows different polysiloxanes to be differentiated from one another. The company tascon – Gesellschaft für Oberflächen und Materialcharakterisierung mbH (tascon – Analytical Services and Consulting) in Münster, offers a corresponding analysis service.

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Droplet contact angle measurement

In order to find out whether residues that could possibly be extracted from the glove matrix through solvent extraction can be removed and transferred to an object surface, we used the comparative droplet contact angle measurement as the sum parameter. Any traces of silicone oil are included but cannot be detected in a material-specific manner.

In the first experiment, a C&C collector plate made of glass was cleaned using diiodomethane and DI water and allowed to dry under cleanroom conditions. The corresponding droplet contact angles for diiodomethane and separately for DI water droplets were then determined. In addition, both the dispersive and the polar surface free energy were calculated for the cleaned glass surface.

In the second experiment, the collector plate was rinsed with 2-propanol and, after drying, the droplet contact angles and the two surface energies were determined again.

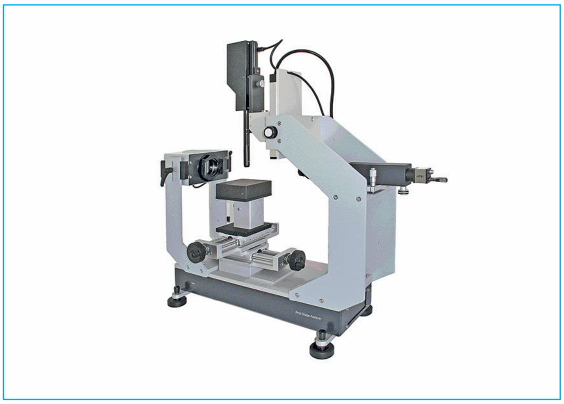

Fig. 8 Droplet contact angle analyzer

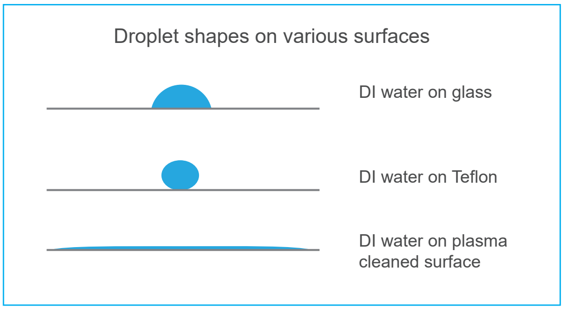

Fig. 9 Droplet shapes on various surfaces

In the third experiment, a PU glove was extracted for 20 minutes in a microwave extraction system. The extraction liquid was then applied to the glass plate and allowed to dry there.

All three experiments described were carried out 12 times in succession to ensure plausibility. The highest and lowest values were eliminated. The results are shown in the table in Fig. 10. For the water droplets, contact angles of 65 ° were found on the pure substrate surface, 61 ° for the 2-propanol-immersed surface and 57 ° for the surface immersed in the extraction liquid. The microwave extraction from the glove matrix resulted in a droplet contact angle change of 4 °. But as stated before: from the data obtained in this way, it is not possible to determine what proportion of the total foreign substances possible silicone compounds have.

In order to obtain first approximation data on which contact angle changes occur when the surface of the object is contaminated, especially with traces of silicone oil, it makes sense to lightly spray a previously highly cleaned glass surface with a silicone-containing aerosol, to then clean this with a wiping agent and measure it again.

As can be seen from Table 1, a glass plate that has been cleaned to a high degree in oxygen plasma can be completely wetted with water. If, on the other hand, the glass plate is cleaned by means of solvents and the action of ultrasound, the result is a droplet contact angle of 59.3 °. The targeted conta-

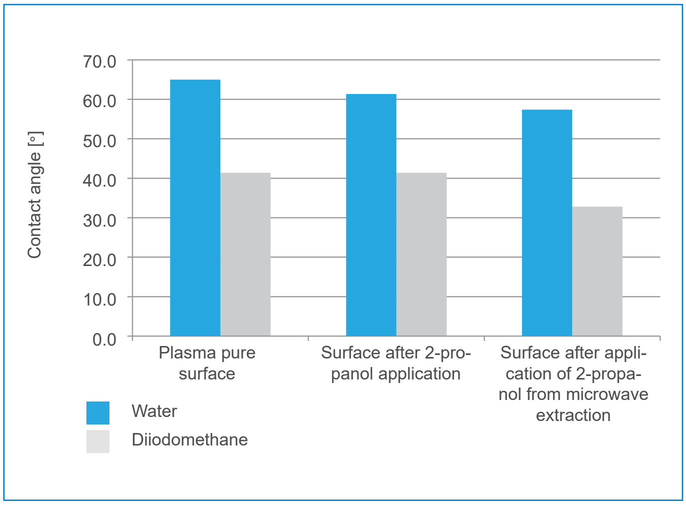

Fig. 10 Change in the contact angle in the context of the droplet shape analysis for the media ultrapure water and diiodomethane.
A) clean surface, B) surface after application of 2-propanol, C) surface after application of 2-propanol from a microwave extraction of a PU glove with traces of silicone oil.

Test method "lying drop"

Young equation

$$\cos \theta = \frac{\delta_S - \delta_{LS}}{\delta_L}$$

δ_L = Surface tension of the liquid
δ_S = Surface energy of the solid
δ_{LS} = Interfacial energy between Liquid and solid
θ = Contact angle

Fig. 11 "Horizontal drop" test method, Young equation

mination of the glass plate with a silicone oil causes a contact angle of 68.4 °.

If the contaminated surface is cleaned by wiping, an acceptable level of cleanliness with a contact angle of less than 60 ° can only be achieved with a solvent-moistened special wipe (test specimen No. 2-1), although all tested surfaces no longer exhibit any *visually visible* streaks.

The visual assessment of a cleaned surface is therefore insufficient to determine the actual surface cleanliness. A target-oriented analytical strategy is important here, especially since silicone oils are optically transparent. A two-stage process is often used for this purpose: First, the purity state is checked directly in the production line using the non-destructive contact angle method. If a certain limit value is not reached, the test item must be sorted out and sent for further analysis to identify the source of contamination (FTIR, ToF-SIMS).

Conclusion

In the clean manufacturing environment for a number of surfaces, in addition to their technically useful property profile, silicone oils have an increased contamination potential, which results from the oil's tendency to creep and its difficult cleanability.

A clear identification of silicone oil traces by means of the widespread droplet contact angle measurement is not possible. In contrast, alternative analysis methods such as FTIR spectroscopy, GCMS or ToF-SIMS are well suited to identify traces of silicone oil. This also applies to the visualization on the Labuda collector plate [6].

Condition of the collector plate:	Droplet edge angle	Difference to the contaminated surface
Unused	81.8 ° ± 2.9%	+ 13.4 °
Purified by low pressure O_2 plasma	<5 °	
Ultrasonically cleaned in acetone	59.3 ° ± 8.4%	- 9.1 °
Contaminated with silicone oil aerosol (reference)	68.4 ° ± 4.6%	± 0.0 °
Cleaned again with test item code 2-5. dry	68.3 ° ± 2.6%	- 0.1 °
Cleaned again with test item code 2-5 and acetone	63.0 ° ± 9.6%	- 5.4 °
Cleaned again with test item code 2-1. dry	71.0 ° ± 4.2%	+ 2.7 °
Cleaned again with test item code 2-1 and acetone	50.9 ° ± 7.1%	- 17.4 °

(low droplet contact angle correlates with high purity)

Table 1 Droplet contact angle as a result of wiping cleaning procedures with high-tech cleaning wipes on glass plates contaminated with silicone oil

Test item code	1-1 V	1-2 V	1-4 V	2-1 G	2-5 G
Textile construction	nonwoven	nonwoven	nonwoven	knitted	knitted
Material type	Cellulose (CEL)	Cellulose (CEL)	Pulp / polyester (CEL / PES)	Polyester / polyamide (PES / PA)	Polyester (PES)
Decontamination	none	none	none	aquatic	aquatic
Basis weight	60 g / m²	72 g / m²	70 g / m²	151 g / m²	147 g / m²
Mesh count	n.a.[1]	n.a[1]	n.a[1]	900 / cm²	380 / cm²
Outgassing, GCMS at 25 ° C, per m² of filament surface	103.9 µg / m²	68.3 µg / m²	n.a.[2]	8.1 µg / m²	25.4 µg / m²
Organic total carbon TOC per HiTech cleaning cloth 23 x 23 cm	1451 µg	5055 µg	1462 µg	2264 µg	628 µg

Table 2 Textile properties and purity parameters of the high-tech cleaning wipes examined in this article. The product names are shown in coded form (see first line).

n / A. not applicable
1: Nonwovens have no textile meshes
2: The surface of the cellulose fibers of the test item 1-4 (V) cannot be determined.

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