

CLEANING OF SILICONE CONTAMINATIONS: DEVELOPMENT OF TEST METHODS AND ASSESSMENT OF CLEANING EFFICIENCY

Volker Liedtke⁽¹⁾, B.D. Dunn⁽²⁾, C. Macho⁽¹⁾, E. Semerad⁽¹⁾

(1) *Austrian Institute of Technology, Aerospace and Advanced Technologies, A-2444 Seibersdorf,
+43 50550 3346, volker.liedtke@ait.ac.at;
+43 50550 3323, christoph.macho@ait.ac.at; +43 50550 3322, ernst.semerad@ait.ac.at*
(2) *European Space Agency, TEC-Q, +31 71 565 3900, barrie.dunn@esa.int*

1 ABSTRACT

Silicones are widespread contaminations in spacecraft, resulting from their ubiquitous utilisation in different manufacturing and assembly steps.

A suitable methodology for assessing the cleaning efficiency had been developed. Measuring the contact angle and calculating the surface energy was found to be 2-3 orders of magnitude more sensitive than FTIR.

Up to now, the most efficient cleaners were commercially available agents specifically designed for silicone removal.

2 INTRODUCTION

Silicone products used for spacecrafts range from oils and greases to cured products as used for sealing materials, adhesives, paints, or conformal coatings. They offer excellent properties, e.g. low vapour pressure and low surface tension (oil lubricants), high thermal conductivity (thermally conductive vacuum greases), chemical inertness, good dielectric properties, and ductility (conformal coatings and paints). Silicones on the other hand can act as major sources of contamination if they are incorrectly handled or used. Their low surface tension will cause oils to creep over clean surfaces, spreading contaminations into gaps and other areas that are almost impossible to clean. Under vacuum, such trapped reservoirs can act as a long-term source for further contamination. Therefore, a thorough removal before launch is mandatory.

For the assessment of contaminant films one has to differentiate between carbon-based (organic) material and silicone-containing material. Organics exposed to atomic oxygen are removed rather rapidly. Exposure to atomic oxygen will cause silicone contaminated surfaces to oxidize to silicates producing a glassy, non-volatile layer. Silicones remaining trapped beneath this surface will darken under UV exposure.

Silicone contamination was extensively studied after the retrieval of the Long Duration Exposure Facility (LDEF), where extremely thin, patchy films of silicone-based contamination were distributed all around the circumference [1]. On leading edge surfaces, it was found that silicones had been oxidized into silicates by

the atomic oxygen. Including the leading edge, a molecular film that contained silicone was revealed. Since this silicone film had not reacted with atomic oxygen to form silicates, it must have been deposited after the surfaces were shielded from atomic oxygen, such as would have occurred when LDEF was re-berthed in the Shuttle. Collectively, there were many sources of silicone contamination on LDEF. Some areas had been contaminated prior to flight, others by silicone-based materials outgassing during flight. This well documented example shows that silicone contamination of spacecrafts is an evident problem and may originate from different sources, including pre-flight exposure, launch, on-orbit and re-entry effects, and post-flight processes.

Potential sources of silicone contamination during pre-flight, launch and post-flight periods may be caused by the use of silicone containing materials of high vapour pressure (e.g. release agents) applied to non spacecraft parts, the curing of silicone based paints, the curing of silicone based conformal coatings (e.g. Solithane), and by direct or indirect contact during handling – a major source for silicone contaminations results from cosmetics that are then transferred to flight hardware or manufacturing tools! In orbit, outgassing of silicone based materials with high outgassing rates and the creep of oils and greases can act as continuous sources for the build up of silicone contaminant films.

Some studies have been performed to evaluate the efficiency of cleaning methods e.g. a systematic study investigating the influence of defined cleaning agents on specially coated metallic surfaces [2] or an evaluation of the effect of new cleaning liquids on electronic materials and parts [3] and conformal coatings [4].

3 EVALUATION OF SILICONE DETECTION METHODS

3.1 Preparation of Test Plates

A solution of 0.5 g DC 200 silicone oil in 49.5 g dichloromethane (Merck, p.a. grade) had been prepared and further diluted to receive solutions with the following weight% of DC 200 in dichloromethane:

$1 \cdot 10^0$, $1 \cdot 10^{-1}$, $1 \cdot 10^{-2}$, $1 \cdot 10^{-3}$, $1 \cdot 10^{-4}$, $1 \cdot 10^{-5}$, $1 \cdot 10^{-6}$, and $1 \cdot 10^{-7}$ weight% Each 4 glass microscopy cover plates were dipped into the respective solution, the excess been shaken off, and then dried in air. As references, each 4 plates directly from the package (labelled “as received”) and dipped into pure dichloromethane (labelled “reference cleaned”) had been prepared. Mass of samples before and after contamination/drying had been recorded with a lab scale with 1 µg resolution.

3.2 Contact Angle Measurement

Contact angle measurements were performed with a Krüss Drop Shape Analysis System DSA 10 Mk 2, using water, ethylene glycol, and diiodomethane as reagents, i.e. as droplets.

When a drop of a liquid is in contact with a solid surface, two types of liquid/solid interactions are to be considered:

- The polar interactions reflect Coulomb interactions between permanent dipoles and between permanent and induced dipoles, as well as hydrogen bonds
- The disperse interactions result from time dependent fluctuations in the charge distribution within the molecules

The total surface energy of the liquid σ_l therefore consists of two contributions:

$$\sigma_l = \sigma_l^d + \sigma_l^p$$

According to the theory of Owens, Wendt, Rabel and Kaelble [5], the surface energy of a solid can be calculated according to

$$\sigma_l * (1 + \cos \Theta) = 2 * (\sqrt{\sigma_l^d \sigma_s^d} + \sqrt{\sigma_l^p \sigma_s^p})$$

Thus, if at least two solvents of different polarity are available, the polar and the dispersive contribution to the surface energy of the solid can be calculated. Using three solvents with different polarity does significantly enhance the accuracy of the measurement.

The surface energies of the three liquids employed within this study are given in Table 1:

Table 1: Surface energies of liquids used for contact angle measurements; all data from common literature

Liquid	σ_p [mN/m]	σ_d [mN/m]	σ [mN/m]
Water	51,0	21,8	72,8
Ethylene glycol	16,8	30,9	47,7
Diiodomethane	2,3	48,5	50,8

More details of the method may be derived from [5]

Measurement procedure: The sample is placed at the sample desk (centre of Fig. 2), a drop is placed onto the sample using the syringe. The digital camera, which is integrated into the device (left), takes pictures of the drop from the side. The software (DSA for Windows) analyses the picture calculates the contact angle. After

measuring the contact angle with two or more liquids, the surface tension of the sample can be calculated using Owens-Wendt-Rabel-Kaelble’s method, as shown in Fig. 1:

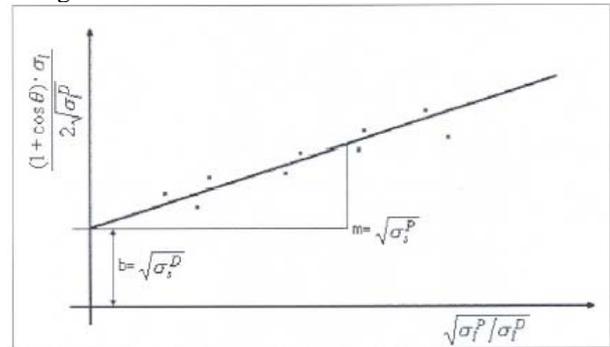


Fig. 1: Evaluation of surface energy by Owens-Wendt-Rabel-Kaelble’s method [5]

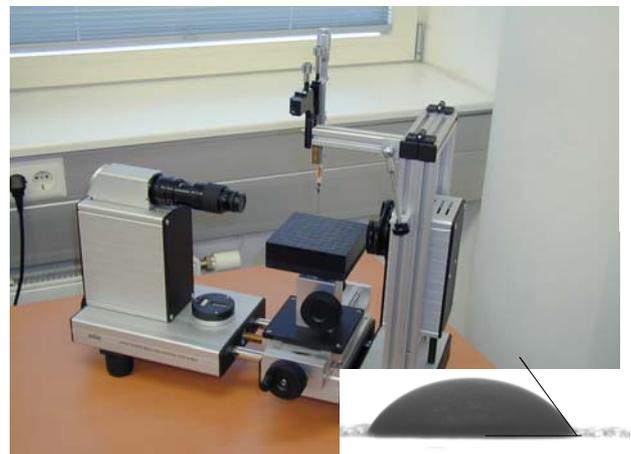


Fig. 2: Krüss Contact Angle Measurement device; bottom right: Droplet with contact angle of 50°

3.3 Fourier Transform Infra-Red (FTIR) Spectroscopy

FTIR spectra were taken with a Bruker Equinox 55 device in diffuse reflection mode. As a reference, the non-contaminated glass plate and the pure contaminant (i.e. DC 200) were measured.

3.4 Results – Silicone layer thickness calculation

The thickness of the layers had been calculated from the mass change of the samples. The resolution of the balance did only allow the measuring of mass change when solutions of at least 10^{-3} weight% were applied. Lower concentrations had to be extrapolated.

With a density of dichloromethane of 1.02 g/cm^3 and a plate area of 11.52 cm^2 , the formula

$$\text{Layer_thickness}_{[cm]} = \frac{\text{Mass_change}_{[g]}}{\text{density}_{[g/cm^3]} * \text{plate_area}_{[cm^2]}}$$

gives the following results, as presented in Table 2:

Table 2: Calculated layer thickness for different concentrations of DC 200 in dichloromethane

Dilution [wt% DC200 in CH ₂ Cl ₂]	Layer thickness [μm]
1,E+00	1,24366
1,E-01	0,14330
1,E-02	0,02362
<i>1,E-03</i>	<i>0,01740</i>

The last value in italics seems already unreliable, as the respective mass change is within the accuracy limits of the balance.

With the first three data sets, an interpolation – taking into account the apparent non-linearity of data, evaporation effects, and the like by applying a correlation coefficient of 1.1 – allows the estimation of layer thicknesses for the diluted solutions, too. This is presented in Fig. 3:

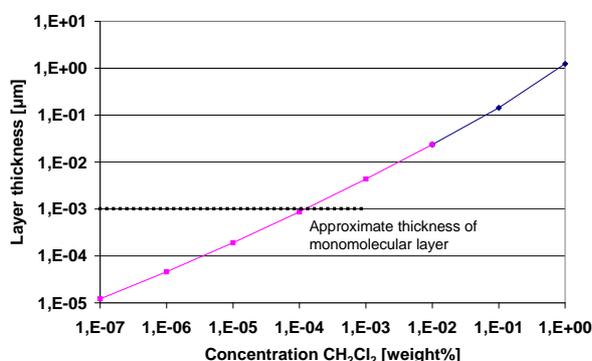


Fig. 3: Extrapolated silicone layer thickness for different concentrations of contaminant

The physical meaning of a layer thickness below the monomolecular layer is an incomplete covering of the sample surface. This implies that a concentration of $1 \cdot 10^{-4}$ wt% silicone results in (theoretically) complete coverage of the surface with a monomolecular layer, and a monomolecular surface coverage of 10% caused by a $1 \cdot 10^{-5}$ wt% silicone solution.

3.5 Results – Contact Angle Measurements

Surface energy and contact angle are presented in the following Fig. 4. Results for DC 200 solutions, for reference (as received) and clean (reference dipped into dichloromethane) are presented.

A plot of the wetting angles with different reagents as a function of (approximated) silicone layer thickness, as shown in Fig. 3, allows an assessment of the minimum layer thickness that can be detected with the contact angle method. These plots are shown in the following Fig. 5; the dotted horizontal lines represent the respective values for the reference samples cleaned with dichloromethane.

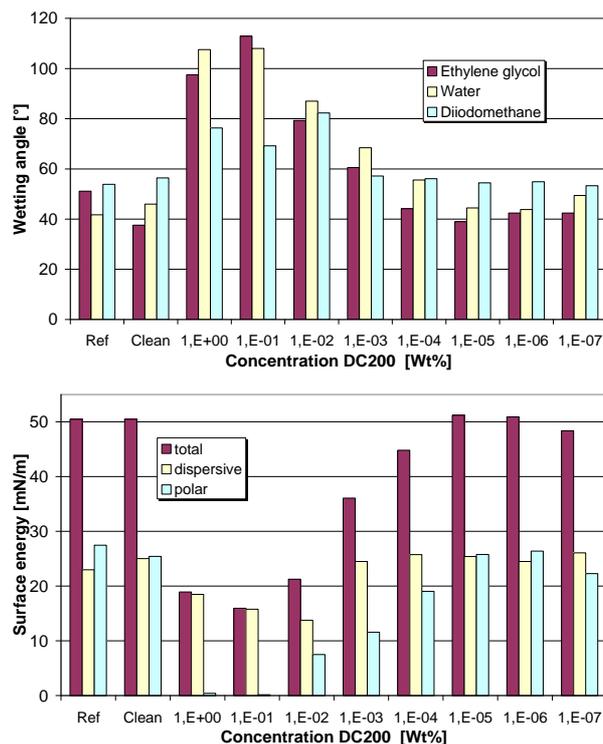


Fig. 4: Contact angle (top) and calculated surface energies for various DC 200 concentrations and for reference samples

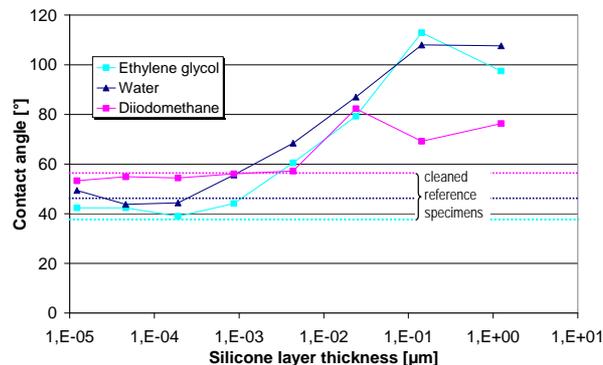


Fig. 5: Contact angle as a function of approximated silicone layer thickness; dotted horizontal lines represent values for cleaned reference specimen

From this plot it can be derived that a layer thickness of $5 \cdot 10^{-3}$ μm seems to be the minimum layer that has a significant influence on the wetting angle and the surface energy of a silicone-contaminated glass plate. This assumption is however based on a number of conditions that may not always be completely fulfilled:

- The layer thickness is estimated to be homogenous over the entire glass plate
- The layer is complete, e.g. there are no spots of unaffected glass surface
- The applied method for estimating the layer thickness is valid

From all these prerequisites, and with a reasonable error consideration for both contamination procedure and contact angle measurement, it shall be stated that the safe detection limit for a silicone contamination by this contact angle method shall not be lower than $1 \cdot 10^{-3} \mu\text{m}$.

3.6 Results – FTIR Measurements

The FTIR measurements of DC 200 silicone, shown in Fig. 6, indicate a peak at around 2960 cm^{-1} , attributed to the aromatic C-H bonds (shifted towards lower wave numbers due to silicon groups at the aromatic system). At higher concentrations, the peaks at 2898 cm^{-1} , from aliphatic $-\text{CH}_2-$ groups, and at 1257 cm^{-1} , representing the Si-C-H bond of the poly-dimethylsiloxane, can also be evaluated despite their overlapping with the broad absorption band of the glass with a maximum at approx. $930\text{-}950 \text{ cm}^{-1}$, as shown in Fig. 7.

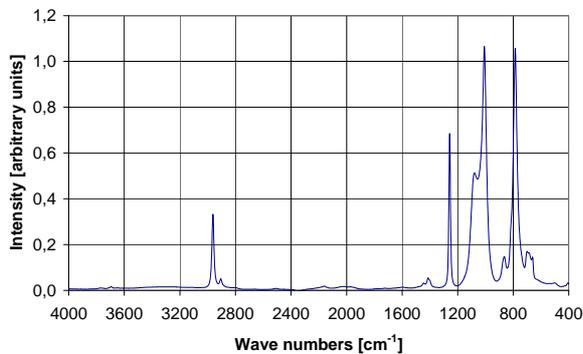


Fig. 6: FTIR spectrum of DC200 silicone oil

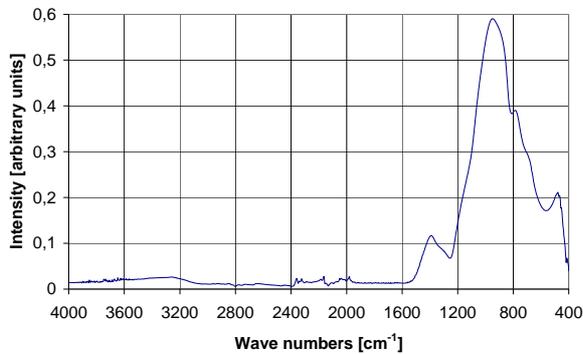


Fig. 7: FTIR spectrum of clean glass substrate

FTIR peak intensities of glass plates contaminated with different dichloromethane solutions are presented in Fig. 8. This diagram reveals the following results:

- For concentrations below 10^{-1} g/l , only the peak at 2960 cm^{-1} can be detected
- The intensity of this peak is almost the same for all concentrations below 10^{-1} g/l , and it cannot be clearly separated from the under-ground noise
- All other peaks cannot be detected at concentrations below 10^{-1} g/l

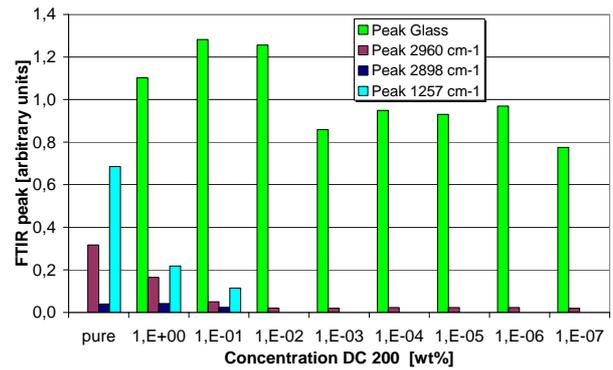


Fig. 8: Intensities of selected absorption bands of the DC 200, and of the glass plates (at $930\text{-}950 \text{ cm}^{-1}$)

A semi-quantitative evaluation, based on the peak intensity ratio of selected absorption bands and the $930\text{-}950 \text{ cm}^{-1}$ glass plate absorption, is shown in Fig. 9:

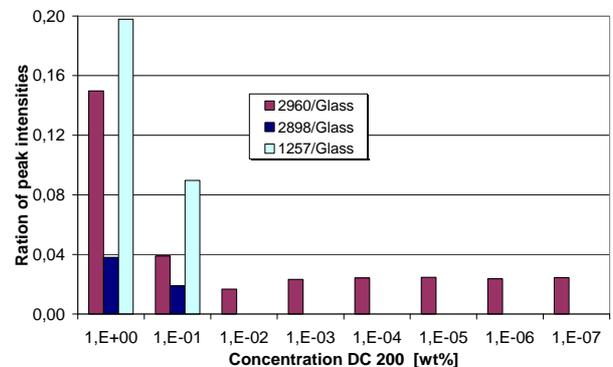


Fig. 9: Ratio of peak intensities; DC 200 peaks normalised by glass absorption band

This underlines the conclusions already drawn from Fig. 8. With results described in Section 3.4, it can be concluded that only layers of more than $0.024 \mu\text{m}$ can be detected by FTIR at all, and that a layer thickness of $0.15 \mu\text{m}$ is required for quantitative evaluation.

3.7 Summary – Silicone Detection Methods

Because of the poor sensitivity of the FTIR method, requiring at least a $2.4 \cdot 10^{-2} \mu\text{m}$ thick silicone contamination on the surface, the only appropriate method for (semi-)quantitative detection of very thin surface layers is the surface angle method.

The sensitivity seems sufficient for safely detecting a layer of $5 \cdot 10^{-3} \mu\text{m}$, making the contact angle method at least 5 times more sensitive than the FTIR method.

The disadvantage is the substantially higher effort for surface angle measurements compared to FTIR measurements.

4 CLEANING OF SILICONE CONTAMINANTS

4.1 Contaminants

The following silicone contaminants, representing typical species that may come into contact with spacecraft, had been selected:

- Poly-dimethylsiloxane oil Dow Corning DC 200
- Pentaphenyl-trimethyl-trisiloxane oil Dow Corning DC 705
- Mould release agent 330 LV Silicone Emulsion from Basildon Chemicals
- Cured silicone resin DC 93-500 from Dow Corning
 - Applied by rubbing on substrate
 - Applied as an extract in tetrachloroethylene
- Thermally conductive vacuum grease DC 340 from Dow Corning

4.2 Cleaning agents

- Methylene chloride CH_2Cl_2 , p.a. (Merck)
- Toluene $\text{C}_6\text{H}_5\text{-CH}_3$, p.a. (Merck)
- n-Hexane C_6H_{14} , p.a. (Merck)
- Fluxclene, manufactured by Electrolube
- Silgest SD0001 (distributed by Polymer Systems Technology Ltd.)
- Ortimex Alkaline Cleaner, distributed by H.C. Stehelin
- SWAS (Safewash Super), manuf. by Electrolube
- Vericlean defluxer (Microcare)
- Vertrel CCA (DuPont, distributed by Microcare)
- Vertrel CMS (DuPont, distributed by Microcare)
- Dowclene 1601 (based on 1-Methoxy-2-propanol) (Dow Chemicals)
- Dowclene PX-16S

4.3 Contamination procedure

To get a thin and uniform layer, a small amount of contaminant was placed on one glass plate, and then distributed by gently moving a second plate against the first one, as depicted in the following Fig. 10:

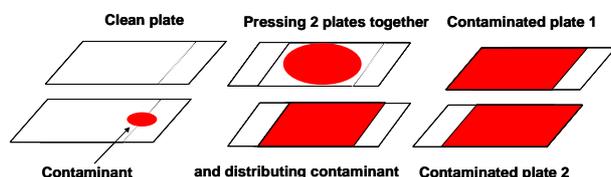


Fig. 10: Schematic view of contamination procedure

4.4 Cleaning of the samples

Cleaning was made immediately after contamination. A standard paper tissue (Kleenex) has been used. The tissues have been moistened with the solvent by pouring

a defined amount of liquid over it. The cleaning was repeated five times for each of the contaminated glass plates, using fresh tissue surface every time.

The direction of cleaning strokes starts always from the not contaminated side of the plate (right of plate 1, left of plate 2, as shown in Fig. 10), to avoid the mobilisation of excess contaminant from the plate edge.

It is important to consider the change of surface polarity by the cleaner itself. Depending on the cleaning agent, relevant changes to the surfaces compared to *as received* plates were observed. This was most obvious for the strong alkaline Ortimex cleaner that was almost “etching” the glass plate surface and resulting in extremely polar surface conditions. To compensate for this, plates directly from the box were subject to the standard cleaning procedure, and all results with the respective cleaners were compared to this baseline.

4.5 Results of first cleaning tests

Results are summarised in Table 3; the symbols for cleaning efficiency mean

- ++ good
- o remaining contaminations
- poor
- + reasonable
- unsuitable

Table 3: Summary of first test series

Designation	330 LV	DC 200	DC 705	DC 93-500 rub	DC 93-500 ext	DC 340
Methylene chloride	++	o	-	-	+	--
Toluene	++	o	+	+	+	-
n-Hexane	+	--	-	-	-	--
Fluxclene	++	-	++	++	++	-
Silgest SD0001	o	+	+	+	+	+
Ortimex	+	--	o	-	o	--
Safewash Super	+	o	+	+	+	-
VeriClean	o	+	+	o	+	-
Vertrel CCA	+	-	--	+	-	--
Vertrel CMS	+	--	o	-	-	--
CH_2Cl_2 /Toluene 1:1	+	-	-	--	-	o
CH_2Cl_2 /n-Hexane 1:1	++	o	+	+	+	-
Dowclene 1601	+	-	o	-	o	--
Dowclene PX-16S	-	-	o	-	-	--

Some of the results were not fully consistent, and reproducibility of the tests was also limited. Scattering between individual test samples – though nominally done under identical condition – was rather large, too. Therefore, a thorough analysis of the entire cleaning process chain, of the reagents and of any other material utilised had been performed. Results of this thorough analysis shall be discussed briefly.

Several possible sources of error could clearly be excluded:

- Performance of tests:
 - No “operator effect” could be identified
- Time between contamination and cleaning
 - Assuming that some kind of curing or other chemical reaction could happen, this time was varied from minutes to days. No differences had been found.

- Room temperature effect
Despite RT varied from 20 to 30 °C during tests, the effect on contact angle measurement was fully compensated by calibration prior to each test.
- Contamination of test plates by dust
Dust particles or flakes from the tissues would be visible during contact angle measurement

Other possible factors were identified that are expected to influence the quality of results:

- Inhomogeneous distribution of contaminant
Mainly for the highly viscous thermal conductive grease DC340, this was a major concern. Despite all efforts, layer thickness could not be fully standardised
- Contact force tissue/sample
Could influence the cleaning efficiency despite use of a sponge to homogenise the load
- Contact angle measurement
Scattering of results could not be improved despite all efforts. The only practical solution could be increasing number of test plates and deleting the highest and lowest values of contact angle
- Tissues used
Commercially available paper tissues from different suppliers and different batches did not give any systematic difference in results. Though not confirmed by tests, surface contaminations from manufacturing process could possibly influence test results
- Glass plates used:
Tests described in Section 3 were made with different plates. Using plates from different suppliers did not give consistently better results. Thorough analyses gave reason to assume that plates – except for the batch used for evaluation of detection methods, described in Section 3 – were coated with a thin silicone layer to avoid their sticking in the package.

4.6 The influence of glass substrate contaminations

The contact angle method shows the polarity of a surface. In the first tests it was assumed that the polar surface of the glass can be attributed to “clean”, while a less polar surface is caused by contaminations. This assumption is based on the chemical structure of most silicones having a “polar” side with siloxane bonds that attach themselves to the polar glass surface, and an unpolar side such as a phenyl group that is being detected by the contact angle measurement.

However if the glass plate should be covered with a very thin layer of silicone from manufacturing, results of the contact angle measurements could even be reversed, with a polar surface now to be attributed to contamination. This is depicted in the following Fig. 11, showing how a silicone layer may actually reverse the expected surface polarity of a contaminated substrate.

Despite the initial assumption that a polar surface can be attributed to a clean plate, it may actually be caused by a

double silicone layer: A layer from manufacturing process and a layer from the intended contamination applied during this study.

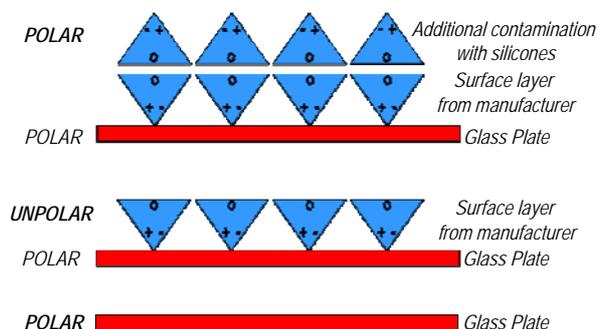


Fig. 11: Surface polarity for various conditions of glass plates: Bottom – clean plate, middle – silicone layer from manufacturing, top – intended contamination

4.7 Improvement of cleaning procedure

Based on the assumptions described in the previous sections, key steps of the procedure were modified.

- Pre-cleaning of sample glass plates
To safely remove any contaminations from the manufacturing process, all plates were treated in a perchloroethylene steam cleaner at 100 °C for 4 h
- Increasing sample size
To get better statistics by measuring at least 10 contact angles with each reagent (water, ethylene glycol, diiodomethane), samples with 40x15 mm² area were used
- Avoiding implausible data points
By deleting highest and lowest contact angle value, the statistical quality of data was significantly improved and the scattering could be narrowed

Furthermore, the required number of cleaning strokes for safely removing the contaminants was systematically evaluated

4.7 Second loop of cleaning tests

In this second loop, all lessons learned and all improvements of the entire procedure were considered. Because of the increasing complexity, the number of contaminants and of cleaning agents had to be restricted:

- Mould release agent Basildon 330 LV
- DC 705 silicone oil, as it contains both aromatic and aliphatic groups
- DC 340 vacuum grease as the most difficult to clean contaminant
- Dichloromethane, as most preceding tests were made with this solvent
- Dowclene 1601, industrial cleaner for silicones
- Dow Corning OS-120, a methylsiloxane azeotrope

Results are summarised in the following diagrams. In all plots, polar and dispersive portions of surface energies are presented, together with the respective error bars. Horizontal lines indicate the polar surface energy of a clean surface with the respective cleaner. If values after 1, 3, or 5 cleaning wipes differ from values obtained for clean surfaces, the surface is deemed contaminated.

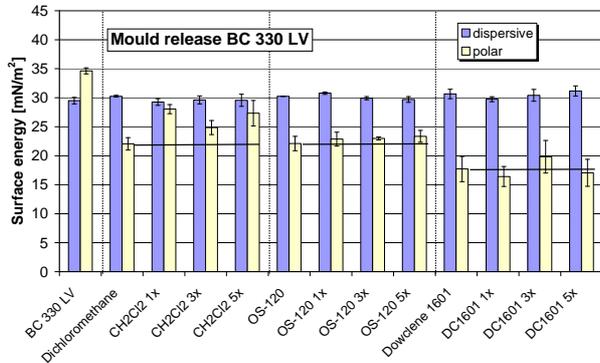


Fig. 12: Surface energies for BC 330, 3 cleaners

Fig. 12 suggests that BC 330 cannot be removed by dichloromethane, as the polar surface energy is always significantly higher than for a clean surface. Both OS-120 and DC-1601 do completely remove the BC330. For OS-120, cleanliness is achieved after a single wipe, while DC-1601 needs 3 wipes to remove it.

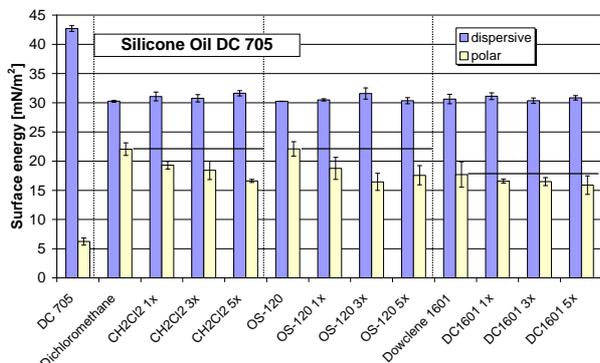


Fig. 13: Surface energies for DC 705, 3 cleaners

Results for this contaminant shown in Fig. 13 indicate that neither dichloromethane nor OS-120 do remove the contamination. For DC-1601, the values for a completely clean surface are not obtained, too, but the differences are almost within the error margin, indicating very little residual contamination.

As presented in Fig. 14, the vacuum grease is the silicone contamination that is most difficult to remove. Dichloromethane and OS-120 cannot remove the grease at all, and more wipes do not improve the cleaning effect. DC-1601 does also not remove this silicone with up to 5 wipes, but more cleaning wipes could further reduce the contamination.

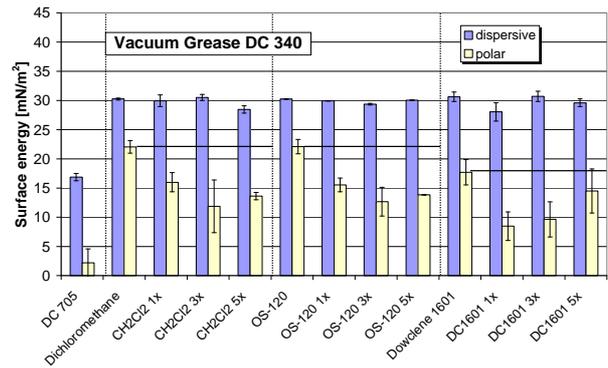


Fig. 14: Surface energies for BC 330, 3 cleaners

5 SUMMARY AND OUTLOOK

In this study it was found that contact angle measurements for calculating the surface energy provide sufficient sensitivity for detecting very thin layers of silicone contaminations on glass surfaces.

Contaminations on the glass plates used, probably originating from the manufacturing, did however cause severe difficulties, and the screening tests could therefore only give indications on suitable chemicals for removing silicones.

In a second loop, the test procedure had further been optimised, and consistent results can now be obtained.

The study shall therefore be continued: First, more cleaners shall be investigated to get a broader database on the ability to remove persistent silicones from glass substrates. Then, the most promising cleaners shall be applied on other substrates that are more relevant for space operations. Typical substrates could include, polymers, PCBs, metals and other surfaces.

6 LITERATURE

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