MAPSIL® QS1123 THIXO-BUV: INTRODUCING A UV INDICATOR TO MAPSIL® QS1123 THIXO-B, AN IMPROVEMENT ON A HIGH HERITAGE SPACE PRODUCT

G. Sierra [(1)], P. Nabarra [(2)], S. Perraud [(2)], D. Sacramento [(1)], M. Cazeneuve [(1)], O. Guillaumon [(1)]

[(1)] MAP SPACE COATINGS, ZI de Bonzom – 1 Rue Paul Maes, 09270 Mazères, France, g.sierra@map-coatings.com
[(2)] CNES – 18 avenue Edouard Belin, 31401 Toulouse Cedex 9, France, Sophie.Perraud@cnes.fr

ABSTRACT

MAPSIL® QS1123 THIXO-B is a low outgassing silicone elastomer developed in the 2010s to ensure thermal management between components in the space industry.

To propose easier inspection, a UV indicator has been added to MAPSIL® QS1123 THIXO-B. Using a UV lamp (λ = 254 nm), the new product, called MAPSIL® QS1123 THIXO-BUV, which is transparent under normal light, turns red.

This paper summarizes the validation tests conducted so far to characterize MAPSIL® QS1123 THIXO-BUV. All the properties were compared to MAPSIL® QS1123 THIXO-B.

1. INTRODUCTION

Since its creation in 1986, MAP has developed numerous products for the space industry. Most of these products are silicone-based greases, adhesives, varnishes or coatings.
MAPSIL® QS1123 THIXO-BUV is a low outgassing silicone elastomer obtained via a solvent-free purification process (patented by CNES) that makes it possible to obtain degassing values compatible with space applications [1].
This product was developed for application on components used in satellite applications to ensure the thermal management between the parts. MAPSIL® QS1123 THIXO-BUV is also used for bonding applications.
To propose easier inspection for quality control, a UV indicator has been added to MAPSIL® QS1123 THIXO-BUV.
The following qualification plan has been defined to check the properties of the new version of MAPSIL® QS1123 THIXO-B:

1. Control of the product in the initial stage and comparison of its properties with the properties of MAPSIL® QS1123 THIXO-B;
2. Aging tests.

This paper first presents the properties of MAPSIL® QS1123 THIXO-BUV in its initial state. These properties are compared to those of MAPSIL® QS1123 THIXO-B. Secondly, the results after aging tests are presented.

2. MATERIALS, PROCESSES AND TECHNIQUES

2.1. Materials

MAPSIL® QS1123 THIXO-BUV is a two-component RTV-2 silicone elastomer. The base is a mix of silicone polymers, pigments and several additives, which gives it its rheological and mechanical properties. The hardener is composed of a mix of additives and a silicone cross-linker to adjust the viscosity. The base and hardener are 100% solid-content products. In order to reach the low outgassing rates as defined by the ECSS [1], a solvent-free purification process was used instead of the purification process based on the use of solvents used until now.

To obtain the final material, the base and hardener must be mixed at a ratio of 10:1 by weight, respectively. The standard curing process corresponds to 7 days at 23°C and 55% relative humidity (RH). The chemical reaction yields a final elastomer. The main characteristics of the current elastomer [2, 3] are listed in Table 1.

Table 1. General properties of current MAPSIL® QS1123 THIXO-B silicone elastomer cured at 23°C and 55% RH for 7 days

Property	Value
Density	1.05
Viscosity at 50 s^{-1} (Pa.s)	26
Pot-life (min) at 20°C	40
Hardness (ShA)	48
TML (%)	0.31
RML (%)	0.30
CVCM (%)	0.01
Electrical surface resistance (Ω/☐)	$>10^{12}$
Electrical resistivity (Ω.cm)	$>10^{12}$

2.2. Techniques

Outgassing rates are measured according to standard ECSS-Q-ST-70-02C [1]. The measurements were taken at Airbus Toulouse.

The linear coefficient of thermal expansion (CTE) of the sample was measured by thermomechanical analysis (TMA) in accordance with standard ISO 11359-2 [4]. This measurement is derived directly from a dilatometer and involves an oven with a sample holding system positioned inside. This system consists of a tray and a silica pusher for standard expansion mode or a setting system tension of samples consisting of a silica frame and two tensioning jaws. These sample gripping systems make it possible to follow the movement of the ends of the sample during a ramp in temperature. It is this displacement measurement that allows the coefficient of thermal expansion to be calculated.
The linear coefficient of thermal expansion was measured using TMA. The measurements were carried out by ELEMCA using a TMA 402 F1 NETZSCH under helium.

Thermal conductivity is measured using the flash laser method. This method is adapted to the measurement of the thermal conductivity of solids [5].
A sample is heated on one of its faces by laser irradiation; on the other side, the temperature is measured as a function of time using a pyrometer. The analysis of the thermogram obtained on the rear face of the sample makes it possible to determine the thermal diffusivity of the sample.
Different models make it possible to analyze these thermograms and to deduce the thermal diffusivity; among them, the simplest is the adiabatic model represented above [5]:

Eq.1 $$a = 0.1388 \ x \ \frac{e^2}{t_{0.5}}$$

Where a is the thermal diffusivity [mm².s^{-1}], e is the thickness of the sample [mm] and $t_{0.5}$ is the “half rise” time, at 50% of the temperature rise of the rear face of the sample [s] (IR sensor side).
The thermal diffusivity measurements are made using a Netzsch LFA 457 diffusivimeter on samples ranging in thickness from 1.2 to 1.9 mm.

Knowing the diffusivity, the value of its conductivity can be determined using the following equation:

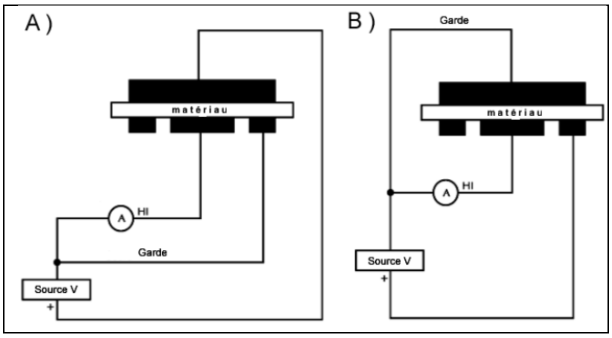
Eq.2 $$\lambda = a \ x \ \rho \ x \ C_p$$

Where λ is the thermal conductivity [W.m^{-1}. K^{-1}] and a is the diffusivity [m². s^{-1}]; ρ and Cp correspond to the density of the sample [kg.m^{-3}] and its mass heat capacity [J.kg^{-1}. K^{-1}], respectively.

The density measurements were carried out by double weighing using Archimede’s principle and the mass heat measurements on a SETARAM calorimeter.
The LIMATB laboratory performed the measurements.

The electrical measurements were carried out according to standard ASTM D257-99 [6] by the LAPLACE lab.
The measuring cell used is of the plane-plane type with a guard electrode (Fig. 1).

Figure 1. Schematic view of (A) electrical resistivity measurement and (B) electrical surface resistance measurement



The measurement method used consists in applying a direct voltage U across the terminals of the sample and measuring the current I traversing it after a defined period of time (1 minute) in order to deduce a resistance R.
The equations for going back to the electrical resistivity are thus as follows:

Eq.3 $$\rho_V = \frac{K_V}{\tau} \times R$$

Eq.4 $$K_V = \pi \frac{(D \times \Phi)^2}{4}$$

Eq.5 $$\rho_V = \frac{2288.1}{\tau\,[mm]} \times \frac{V}{I}$$

Where ρ_V = electrical resistivity [Ω.cm]; $\boldsymbol{\tau}$ = average thickness of the shielding material [mm]; R = electrical resistance [Ω]; D = 2.125 inch; $\boldsymbol{\Phi}$ = 1 inch; V = voltage [V]; I = current intensity measured after 1 minute [A].

Regarding the electrical surface resistance calculation, the following equations were used:

Eq.6 $$\rho_S = \frac{P}{g} \times R$$

Eq.7 $$P = D_0 \times \pi$$

Eq.8 $$\rho_S = 53.4 \times \frac{V}{I}$$

Where ρ_S = electrical surface resistance [Ω/☐]; g = 0.125 inch; R = electrical resistance [Ω]; D_0 = 2.125 inch; V = voltage [V]; I = current intensity measured after 1 minute [A].

The measuring equipment consists of a Keithley 6517B electrometer and a Keithley 8009 test cell. All the measurements were carried out at 100 VDC, the current readings having been made after 1 minute.

The dielectric strength measurements for AC 50 Hz were carried out on samples in the form of films with a thickness of about 100 µm and a diameter of about 40 mm.

The measurements concern the maximumdielectric strength voltage for AC 50 Hz. The samples are placed between two sphere electrodes (diameter: 10 mm) and are connected to a variable AC voltage source between 0 and 80 kV, generated by a BAUR DPA 75C type device. The set (electrodes + equipment tested) is immersed in an insulating fluid (Galden HT55) to avoid bypass phenomena.
The voltage applied between these two electrodes is progressively increased (at a ramp rate of 1 kV/s) until the maximum withstand voltage is reached, a value that will be recorded.
The test is performed at room temperature (25°C).

The following samples were taken to perform the permittivity measurements and to determine the dielectric loss factor:
- Film deposition on aluminum plates measuring 40 mm x 40 mm.
- Gold plating, 28 mm in diameter, was performed on the opposite side (see Fig. 4a).

The dielectric constants and dissipation factors are measured for frequencies of 100 Hz and 100 kHz.

All the other characteristics were measured in-house by MAP further to the following ISO standards, which are included in the reference section:

- Density using a pycnometer [7];
- Viscosity and pot-life using an RS1 rheometer, Thermofisher [8];
- Hardness [9];
- Tensile stress [10];
- Young modulus using DMA [11];
- Tg using DSC [12].

3. QUALIFICATION PLAN

To qualify the new version of MAPSIL® QS1123 THIXO-BUV, its characteristics must meet the requirements listed in Table 2. These requirements come from the characteristics of the current MAPSIL® QS1123 THIXO-B and from the ECSS-Q-ST-70-02C outgassing standard [1].

Table 2. Requirements for MAPSIL® QS1123 THIXO-BUV silicone resin

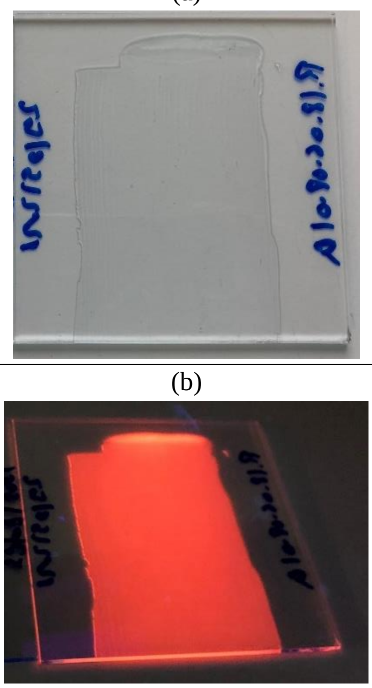
Properties	Requirements
Thermal conductivity ($W.m^{-1}.K^{-1}$)	0.14 – 0.18
RML (%)	≤ 1
CVCM (%)	< 0.1

The characterization of the products was performed at the initial state for all the characteristics: rheological, mechanical, outgassing, electrical and thermal properties.
Some of the characteristics were characterized after a damp heat test (7 days at 50°C and 95% RH) and after a cumulative damp heat test + thermal cycling (90 cycles between -170°C and 130°C under N_2 atmosphere).

4. RESULTS

MAPSIL® QS1123 THIXO-BUV is transparent when cured in low thickness, under 300 µm (Fig. 2a). When using a UV lamp at a wavelength of 254 nm, MAPSIL® QS1123 THIXO-BUV turns red (Fig. 2b). The color can vary depending on the substrate.

Figure 2. MAPSIL® QS1123 THIXO-BUV applied to glass. (a) Under standard light and (b) illuminated with a UV lamp at 254 nm



4.1. INITIAL STATE

4.1.1. GENERAL PROPERTIES

The density of MAPSIL® QS1123 THIXO-BUV was measured using a pycnometer in accordance with standard ISO 2811-1 [7]. The value was measured at 1.05.

The outgassing properties were measured at the Airbus Toulouse facility on a product after 7 days of curing at 23°C and 55% RH. The results are listed in Table 3 [13].

Table 3. Outgassing results for MAPSIL® QS1123 THIXO-BUV

	TML (%)	RML (%)	CVCM (%)
MAPSIL® QS1123 THIXO-BUV	0.37	0.34	0.01
MAPSIL® QS1123 THIXO-B	0.31	0.30	0.01

4.1.2. RHEOLOGICAL PROPERTIES

The values of the viscosity measurements are listed in Table 4. The viscosity of the new version of the hardener is close to that of the current one. A slight increase in the viscosity was observed with regard to the base. Nevertheless, the viscosity of the mix remains close to that of the former one.

Table 4. Viscosity measurements for MAPSIL® QS1123 THIXO-BUV silicon resin

	Base
Viscosity at 50 s^{-1} (Pa. s) and 23°C	26.5

The pot-life was kept at an identical value of 55 minutes at 23°C.

4.1.3. MECHANICAL PROPERTIES

The hardness of MAPSIL® QS1123 THIXO-BUV was measured in accordance with standard ISO 7619-1. The hardness value for MAPSIL® QS1123 THIXO-BUV is 52 Shore A whereas it is around 48 Shore A for MAPSIL® QS1123 THIXO-B (Table 1).

The tensile strength was measured at 5.0 MPa with an elongation at break of 260%. These measurements were conducted in accordance with standard ISO 37.

To evaluate the adhesion properties of MAPSIL® QS1123 THIXO-BUV, lap-shear tests were carried out using PSX primer [14] in accordance with the MAP internal procedure [15] based on standard NF EN 1465 [16]. 2024-T3 aluminum samples of 1.6 mm thick were used. The average thickness of the adhesive used was 131 ± 7 µm. The tensile-shear strength was around 6.3 MPa (Table 6) with cohesive type failures.

The Young modulus was measured using Dynamic Mechanical Analysis (Fig. 3). A value of 1.9 MPa was measured for a curing process of 7 days at 23°C and 55% RH.

The linear coefficient of thermal expansion was measured using TMA. The results are plotted in Table 5 [17].

Table 5. Linear coefficient of thermal expansion of the current and the new versions of MAPSIL® 213 BUV

T (°C)	CTE (10^{-6} K^{-1})
-150 to -120°C	40
-110 to -85°C	459
-70 to -47°C	216
-24 to 255°C	316

The mechanical properties for current and new versions of MAPSIL® QS1123 THIXO-BUV BV are summarized in Table 6.

Table 6. Mechanical properties of MAPSIL® QS1123 THIXO-BUV and MAPSIL QS1123 THIXO-B after curing at 23°C and 55% RH for 7 days

Property	MAPSIL® QS1123 THIXO-BUV	MAPSIL® QS1123 THIXO-B
Hardness (ShA)	52	48
Tensile stress (MPa)	5.0	5.0
Elongation at break (%)	260	250
Tensile-shear stress (MPa) with PSX	6.3	6.0
Young's modulus	1.9	1.2

4.1.4. ELECTRICAL PROPERTIES

MAPSIL® QS1123 THIXO-BUV is an electrical insulating material. The electrical properties are listed in Table 5 below [18-20].

For the dielectric strength, all samples have a clearly identified breakdown point, located towards the center of the sample. The dielectric strength value corresponds to the Weibull analysis, which consists in statistical treatment of all the values measured.

Table 7. Electrical properties of MAPSIL® QS1123 THIXO-BUV and MAPSIL® QS1123 THIXO-B cured for 7 days at 23°C and 55% RH

	MAPSIL® QS1123 THIXO-BUV	MAPSIL® QS1123 THIXO-B
Dielectric strength ($kV.mm^{-1}$)	57.6	-
Dielectric constant at 100 Hz	3.1	3.1
Dielectric constant at 100 kHz	3.0	3.1
Dissipation factor at 100 Hz	6.4×10^{-3}	8.5×10^{-3}
Dissipation factor at 100 kHz	1.1×10^{-2}	8.3×10^{-4}
Electrical volume resistivity (Ω.cm)	5.5×10^{15}	6.5×10^{12}
Electrical surface resistance (Ω/☐)	1.3×10^{16}	2.0×10^{12}

4.1.5. THERMAL PROPERTIES

Thermal conductivity was measured further to the flash laser method.
The Cp is 1.45 $kJ.kg^{-1}$. K^{-1} and the density is 1088 $kg.m^{-3}$. The thermal diffusivity is 0.099 $mm^2.s^{-1}$.
Using equation 2, the average thermal diffusivity was 0.16 $W.m^{-1}$. K^{-1} [21].
The Tg was measured using DSC. The value was close to -123°C for MAPSIL® QS1123 THIXO-BUV.

4.2. AFTER AGING TESTS

Aging tests were carried out at the CNES facility for the current and the new versions of MAPSIL® QS1123 THIXO-BUV. A damp heat test was conducted at 50°C and 95% RH for 7 days. Additional thermal cycling tests were performed under N_2 atmosphere. Ninety cycles were performed between -178.5°C and 136.4°C with a 10-minute plateau at high and low temperatures (gradient = 5°C/min).
The results are shown in Table 8.
One may observe a slight increase in the tensile-shear stress after a damp heat test and cumulative thermal cycling. This was generally observed for such materials due to post-curing when submitting the materials at high temperatures.

Table 8. Mechanical properties at the initial state and after aging tests – New version of MAPSIL® QS1123 THIXO-BUV cured for 7 days at 23°C and 55% RH

	Initial state	After damp heat test	After damp heat test + Thermal cycling
Tensile-shear stress (MPa) with PSX	6.3	7.0	7.8
Failure mode	Cohesive	Cohesive	Cohesive

5. CONCLUSION

A UV indicator has been added to MAPSIL® QS1123 THIXO-BUV for inspection. In the initial state, all the properties of MAPSIL® QS1123 THIXO-BUV are similar to those of MAPSIL® QS1123 THIXO-B. The outgassing properties and tensile-shear stress characteristics remained the same for the new version of MAPSIL® QS1123 THIXO-B.

Tensile-shear stress remained the same after the aging tests (damp heat test and cumulative thermal cycling).

6. REFERENCES

1. ECSS-Q-ST-70-02C, Thermal vacuum outgassing test for the screening of space materials, 2008
2. Qualification of MAPSIL QS1123 THIXO-B adhesive, CNES report, DCT/TV/TH/NT12-12102, December 12, 2012;
3. MAP, Technical data sheet – MAPSIL QS1123 THIXO-B
4. International standard ISO 11359-2, Plastics — Thermomechanical analysis (TMA) — Part 2: Determination of coefficient of linear thermal expansion and glass transition temperature, 1999
5. W.I. PARKER, R.J. JENKINS, C.P. BUTLER, G.L. ABBOTT, Method of Determining Thermal Diffusivity, Heat Capacity and Thermal Conductivity, Journal of Applied Physics 32, 1961
6. ASTM D257-99 standard, Standard Test Methods for DC Resistance or Conductance of Insulating Materials, 2007
7. ISO2811-1 standard, Paints and varnishes – Determination of density – Part 1: Pycnometer method, 2011
8. International standard ISO 3219, Plastics – Polymers/resins in the liquid state or as emulsions or dispersions – Determination of viscosity using a rotational viscometer with defined shear rate, 1994
9. Standard NF ISO7619-1, Rubber, vulcanized or thermoplastic — Determination of indentation hardness — Part 1: Durometer method (Shore hardness), 2006
10. Standard NF ISO 37, Rubber, vulcanized or thermoplastic — Determination of tensile stress-strain properties, 2012
11. Dynamic Mechanical analysis – Young modulus measurement, Mettler Toledo technical document,
12. International standard ISO 11357-2, Plastics — Differential scanning calorimetry (DSC) — Part 2: Determination of glass transition temperature, 1999
13. Outgassing report, Airbus Silicone Adhesive R.18.06.08d, 2021
14. MAP, Technical data sheet – PSX
15. MAP Internal procedure for lap-shear bonding, Reference PA026
16. Standard NF EN 1465, Adhesives — Determination of tensile lap-shear strength of bonded assemblies, 2009
17. Measurement of coefficient of thermal expansion, ELEMCA report, “21T079cR01v1,” 2021
18. Measurement of electrical surface resistance and electrical resistivity, LAPLACE report, “2021.06.03_MAP_Resistivite,” 2021
19. Permittivity measurement and dielectric loss factor, LAPLACE report, “2021.06.03_MAP_Spectro,” 2021
20. Dielectric strength measurements in AC 50Hz, LAPLACE report, “2021.06.03_MAP_Rigidite,” 2021
21. Measurement of thermal conductivity, LIMATB report, “Rapport MAP_septembre 2021,” 2021