MAPSIL® 213-BUV: INTRODUCING A UV INDICATOR TO MAPSIL® 213-B, AN IMPROVEMENT ON A HIGH HERITAGE SPACE PRODUCT

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ABSTRACT

MAPSIL® 213-B is a low outgassing silicone varnish developed in the 1980s to protect printed circuit boards (PCB) and specific materials (Mylar, composites, etc.) from humidity, vibration, and atomic oxygen (ATOX).

To propose easier inspection, a UV indicator has been added to MAPSIL® 213-B. Using a UV lamp (λ = 254 nm), the new product, called MAPSIL® 213-BUV, which is transparent under normal light, turns red.

This paper summarizes the validation tests conducted so far to characterize MAPSIL® 213-BUV. All the properties were compared to the current version of MAPSIL® 213-B.

1. INTRODUCTION

Since its creation in 1986, MAP has developed numerous products for the space industry. Most of these products are silicone-based adhesives, varnishes, or coatings.
MAPSIL® 213-B is a low outgassing silicone resin or varnish obtained via a solvent-free purification process that makes it possible to obtain degassing values compatible with space applications [1]. This product was developed to be applied to printed circuit boards (PCB) and electronic components.
To propose easier inspection for quality control, a UV indicator has been added to MAPSIL® 213-B.
The following qualification plan has been defined to check the properties of the new version of MAPSIL® 213-B:

1. Control of the product in the initial stage and comparison of the properties of the new version of MAPSIL® 213-B with the current one;
2. Aging tests.

This paper first presents the properties of the new version of MAPSIL® 213-B in its initial state. These properties are compared to those of the current version. Secondly, the results after aging tests are presented.

2. MATERIALS, PROCESSES, AND TECHNIQUES

2.1. Materials

MAPSIL® 213-BUV is a two-component RTV-2 silicone elastomer. The base is composed of silicone polymers, a UV indicator, and a catalyst. The hardener is composed of a mix of silicone polymers and a cross-linker. The base and hardener are 100% solid-content products. A solvent-free purification process is used to reach the low outgassing rates defined by the ECSS [1].

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 (1) 7 days at 23°C and 55% relative humidity (RH), whereas an alternative is (2) 4h of pre-curing at 25°C + 12h at 65°C. The chemical reaction yields a final elastomer. The main characteristics of the current elastomer [3] are listed in Table 1.

Table 1. General properties of the current MAPSIL® 213-B silicone varnish cured at 23°C and 55% RH for at least 24 hours

TML (%)	0.37
RML (%)	0.36
CVCM (%)	0.04
Adhesion on PCB with PSX	Class 0

PSX primer is used on aluminum and PCB substrates to improve adhesion and to obtain adhesion characteristics (Class 0) in compliance with standard ISO 2409 [4]. PSX primer was applied using a spray gun in accordance with the indications mentioned in the TDS [5].
The PCB samples were then prepared in accordance with the following steps:

1. Degreasing with isopropyl alcohol;
2. Application of PSX primer with a spray gun in accordance with the parameters defined in the TDS [5];

3. MAPSIL® 213-BUV application by brush according to the TDS [6].

Arlon 35N PCBs from Systronic – Cimulec were used [7]. The thickness of the coatings was around 300 µm.

2.2. Techniques

Outgassing rates are measured in accordance with standard ECSS-Q-ST-70-02C [1]. The measurements were taken at ELEMCA.

Inspection of the cured MAPSIL® 213-BUV can be performed using a UV lamp at a wavelength of 254 nm.

The linear coefficient of thermal expansion (CTE) of the sample was measured by thermomechanical analysis (TMA) in accordance with standard ISO 11359-2 [8]. 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 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.

Thermal conductivity is measured using the flash laser method. This method is adapted to the measurement of the thermal conductivity of solids [9].
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:

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:

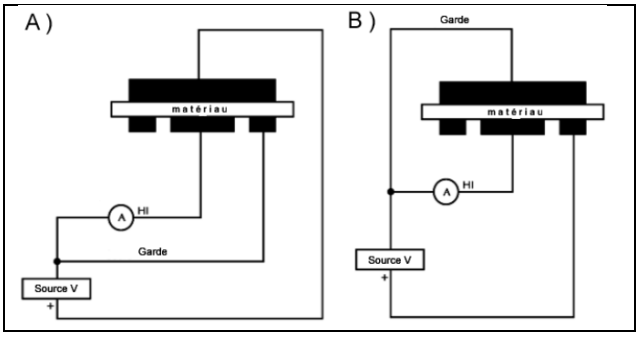
Eq.2 $$\lambda = a\ x\ \rho\ x\ C_p$$

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 Archimedes' principle and the mass heat measurements on a SETARAM calorimeter.
The LIMATB laboratory performed the measurements.

The electrical measurements were carried out in accordance with standard ASTM D257-99 [10] 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 maximum dielectric 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 [11];
- Viscosity and pot-life using an RS1 rheometer, Thermofisher [12];
- Adhesion in accordance with standard ISO 2409 [4].
- Hardness [13];
- Young modulus using DMA [14].

3. QUALIFICATION PLAN

To qualify MAPSIL® 213-BUV, its characteristics must meet the requirements listed in Table 2. These requirements come from the characteristics of the current MAPSIL® 213-B and from the ECSS-Q-ST-70-02C outgassing standard [1].

Table 2. Requirements for MAPSIL® 213-BUV silicone resin

Properties	Requirements
RML (%)	≤ 1
CVCM (%)	< 0.1
Adhesion on PCB with PSX primer	Class 0

The characterization of the products was performed at the initial state for all the characteristics: rheological, outgassing, and electrical properties.
Some of the characteristics were recorded after a damp heat test (7 days at 50°C and 95% RH) and after a cumulative damp heat test + thermal cycling in a vacuum (10 cycles between -170°C and 130°C under N_2 atmosphere) + thermal cycling at atmospheric pressure

(90 cycles between -170°C and 130°C under N_2 atmosphere).

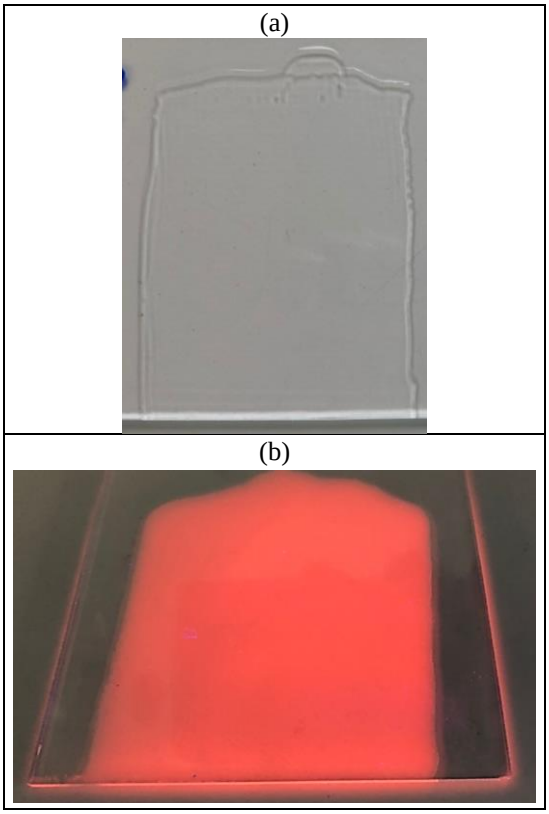
4. RESULTS

4.1. INITIAL STATE

4.1.1. GENERAL PROPERTIES

MAPSIL® 213-BUV is transparent when cured (Fig. 2a). MAPSIL® 213-BUV turns red under a UV lamp at a wavelength of 254 nm (Fig. 2b). The color can vary depending on the substrate.

Figure 2. MAPSIL® 213-BUV applied to glass. (a) Under standard light and (b) illuminated with a UV lamp at 254 nm.



Once cured, the density of MAPSIL® 213-BUV is 1.01.

The outgassing properties were measured at Elemca on a product after 7 days of curing at 23°C and 55% relative hygrometry. The results are listed in Table 3 [15].

Table 3. Outgassing results for MAPSIL® 213-B and MAPSIL® 213-BUV cured for 7 days at 23°C and 55% RH

	TML (%)	RML (%)	CVCM (%)
MAPSIL® 213-B	0.37	0.36	0.04
MAPSIL® 213-BUV	0.40	0.39	0.00

4.1.2. RHEOLOGICAL PROPERTIES

The values of the viscosity measurements are listed in Table 4. The viscosity of the base of MAPSIL® 213-BUV (3.4 Pa.s) is close to that of the current MAPSIL® 213-B (3.6 Pa.s). The viscosity of the mix (Base / Hardener) of MAPSIL® 213-BUV remains close to that of MAPSIL® 213.

Table 4. Viscosity measurements for MAPSIL® 213 BUV silicon resin

	Base	Mix
Viscosity at 50 s^{-1} (Pa. s) and 23°C	3.4	2.5

The pot-life was kept at an identical value of 30 minutes at 23°C.

4.1.3. ADHESION

For MAPSIL® 213-BUV, adhesion was measured in accordance with standard ISO 2409. The measurements were carried out on aluminum and PCB samples after the application of PSX primer. The adhesion values are Class 0, which relates to very good adhesion. These values are the same as those obtained for MAPSIL® 213-B.

4.1.4. MECHANICAL PROPERTIES

The hardness of MAPSIL® 213-BUV was measured in accordance with standard ISO 7619-1 [13]. The value is 35 Shore A whereas it was around 37 for MAPSIL® 213 B (Table 5).

Young's modulus was measured using Dynamic Mechanical Analysis. A value of 0.9 MPa was measured for a curing process at room temperature (7 days).

Table 5. Mechanical properties of MAPSIL® 213 BUV for 7 days in curing conditions at 23°C

Hardness (ShA)	35
Young's modulus	0.9

The linear coefficient of thermal expansion was measured using TMA. The results are plotted in Table 6 [16].

Table 6. 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 -125°C	99
-70 to -55	310
-25 to 255	320

4.1.5. ELECTRICAL PROPERTIES

MAPSIL® 213-BUV is an electrical insulating material. The electrical properties are listed in Table 7 below [17-19].

For the dielectric strength, all samples have a clearly identified breakdown point, located toward 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® 213-BUV cured for 7 days at 23°C and 55% RH

	MAPSIL® 213-BUV	MAPSIL® 213-B
Dielectric strength ($kV.mm^{-1}$)	61.0	86.4
Dielectric constant at 100 Hz	3.0	2.3
Dielectric constant at 100 kHz	3.0	2.2
Dissipation factor at 100 Hz	4.6×10^{-3}	2.4×10^{-3}
Dissipation factor at 100 kHz	4.0×10^{-3}	3.2×10^{-3}
Electrical volume resistivity (Ω.cm)	1.78×10^{14}	1.14×10^{15}
Electrical surface resistance (Ω/□)	9.2×10^{14}	2.87×10^{14}

4.1.6. THERMAL PROPERTIES

Thermal conductivity was measured in accordance with the laser flash method.
The Cp is 1.55 $kJ.kg^{-1}$. K^{-1} and the density is 1.009 $kg.m^{-3}$. The thermal diffusivity is 0.076 $mm^2.s^{-1}$.
Using equation 2, the average thermal diffusivity was 0.12 $W.m^{-1}$. K^{-1} [20].

4.2. AFTER AGING TESTS

Aging tests were carried out at the CNES facility for MAPSIL® 213-BUV. A damp heat test was conducted at 50°C and 95% RH for 7 days. Additional thermal cycling tests were performed in two steps:

1. Thermal cycling tests in a vacuum. 10 cycles were performed between -174°C and 132°C with a 10-minute plateau at high and low temperatures (gradient = 5°C/min);
2. Thermal cycling tests were performed under N_2 atmosphere. 90 cycles were performed between -174.5°C and 133°C with a 10-minute plateau at high and low temperatures (gradient = 5°C/min).

The results are shown in Table 8. The adhesion of the coatings is Class 0 / 5and does not evolve during the aging test.

Table 8. Adhesion characteristics of MAPSIL® 213-BUV in the initial state and after aging tests – MAPSIL® 213-BUV cured for 7 days at 23°C and 55% RH

MAPSIL® 213-BUV	Initial state	After damp heat test	After damp heat test + Thermal cycling
Adhesion	0 / 5	0 / 5	0 / 5

5. CONCLUSION

A UV indicator has been added to MAPSIL® 213-B for inspection. In the initial state, all the properties of MAPSIL® 213-BUV are like those of MAPSIL® 213-B. The outgassing properties and adhesion characteristics remained the same for the new version of MAPSIL® 213-B.
Adhesion 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 adhesives and potting resins produced by MAP, CNES report, 89/CT/DRT/TVE/TH no. 074, February 7, 1989;

3. MAP, Technical data sheet – MAPSIL® 213-B
4. International Standard ISO 2409, Paints and varnishes - Cross-cut test, 2007
5. MAP, Technical data sheet – PSX
6. MAP, Technical data sheet – MAPSIL® 213-BUV
7. Arlon 35N technical datasheet
8. International Standard ISO 11359-2, Plastics — Thermomechanical analysis (TMA) — Part 2: Determination of coefficient of linear thermal expansion and glass transition temperature, 1999
9. 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
10. Standard ASTM D257-99, Standard Test Methods for DC Resistance or Conductance of Insulating Materials, 2007
11. International Standard ISO2811-1, Paints and varnishes – Determination of density – Part 1: Pycnometer method, 2011
12. 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
13. Standard NF ISO 7619-1, Rubber, vulcanized or thermoplastic — Determination of indentation hardness — Part 1: Durometer method (Shore hardness), 2006
14. Dynamic Mechanical analysis – Young modulus measurement, Mettler Toledo technical document,
15. Outgassing report, Elemca 21T184c, 12 05 2021
16. Measurement of coefficient of thermal expansion, ELEMCA report, “21T079cR01v1,” 2021
17. Measurement of electrical surface resistance and electrical resistivity, LAPLACE report, “2021.06.03_MAP_Resistivite,” 2021
18. Permittivity measurement and dielectric loss factor, LAPLACE report, “2021.06.03_MAP_Spectro,” 2021
19. Dielectric strength measurements in AC 50Hz, LAPLACE report, “2021.06.03_MAP_Rigidite,” 2021
20. Measurement of thermal conductivity, LIMATB report, “Rapport MAP_septembre 2021,” 2021