MAP® ATOX 41-BUV: INTRODUCING A UV INDICATOR TO MAP® ATOX 41-B, AN IMPROVEMENT ON A HIGH HERITAGE SPACE PRODUCT

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

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

ABSTRACT

MAP® ATOX 41-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 MAP® ATOX 41-B. Using a UV lamp (λ = 254 nm), the new product, called MAP® ATOX 41-BUV, which is transparent under normal light, turns red.

This paper summarizes the validation tests that have been done so far to characterize MAP® ATOX 41-BUV. All the properties were compared to the current version of MAP® ATOX 41-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.
MAP® ATOX 41-B is a low outgassing silicone varnish 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 to be sprayed on printed circuit boards (PCB) and electronic components. The sprayable property is obtained thanks to the use of a thinner.
To propose easier inspection for quality control, a UV indicator has been added to MAP® ATOX 41-B.
In order to check the properties of the new version of MAP® ATOX 41-B, we have defined the following qualification plan:

1. Control of the product in the initial stage and comparison of the properties of the new version of MAP® ATOX 41-B with the current one;
2. Aging tests.

This paper first presents the properties of the new version of MAP® ATOX 41-B in the 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

MAP® ATOX 41-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 silicone of polymers and a cross-linker. The base and hardener are 100% solid-content products. To reach the low outgassing rates defined by the ECSS [1], a solvent-free purification process is used.

To obtain the final material, it is necessary to mix the base and the hardener in the respective weight proportions of 100 to 10. The mix is then diluted with the thinner in a weight ratio varying from 75% to 85%. The standard curing process corresponds to (1) 7 days at 23°C and 55% relative hygrometry (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 [2-4] are listed in Table 1.

Table 1. General properties of the current MAP® ATOX 41-B (MAPSIL® QS Thinner) silicone varnish cured at 23°C and 55% RH for at least 24 hours

TML (%)	0.54
RML (%)	0.52
CVCM (%)	0.02
Electrical surface resistance (Ω/□)	$>10^{14}$

PSX primer is used on aluminum and PCB substrates to improve adhesion and to obtain compliant adhesion (0 class) compliant with the ISO 2409 standard [5]. PSX primer was applied according to the indications mentioned on the TDS [6] using spray gun pulverization. The PCB samples were then prepared according to the steps hereunder:

1. Degreasing with isopropyl alcohol;

2. PSX primer application using spray gun pulverization with the parameters defined on the TDS [5];
3. MAP® ATOX 41-BUV application with spray gun pulverization according to the TDS [4].

Arlon 35N PCBs from Systronic – Cimulec were used [7]. The thickness of the coatings was around 20 µm.

2.2. Techniques

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

Inspection of the cured MAP® ATOX 41-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) according to the ISO11359-2 standard [8]. This means of measurement is directly derived 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 jaws in tension mode. These systems of gripping the samples 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 calculation of the coefficient of thermal expansion.
The linear coefficient of thermal expansion was measured using TMA. The measurements were carried out by ELEMCA using a TMA 402 F1 NETZCH.

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, a measurement of temperature as a function of time is carried out by pyrometry. 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, we may go back to the value of its conductivity using the following equation:

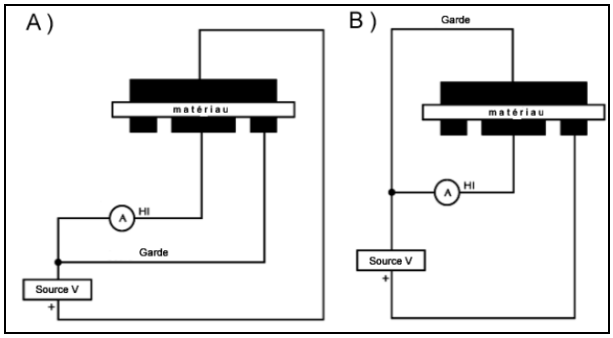
Eq.2 $$\lambda = a\ x\ \rho\ x\ C_p$$

Where λ is the thermal conductivity [W.m^{-1}. K^{-1}] and a 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 measurements were performed by LIMATB laboratory.

The electrical measurements were carried out according to the ASTM D257-99 standard [10] by 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 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 is composed of a Keithley 6517B electrometer as well as a Keithley 8009 test cell. All the measurements were carried out at 100 VDC, the current having been taken up after 1 minute.

The measurements of dielectric strength in 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 voltage of dielectric strength in 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 + tested material) 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).

To perform the permittivity measurements and the dielectric loss factor, the following samples were made:

- 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 SPACE COATINGS according to the following ISO standards, which are included in the reference section:

- Viscosity and pot-life using AFNOR cups [11];
- Adhesion according to the ISO 2409 standard [5].

3. QUALIFICATION PLAN

To qualify MAP® ATOX 41-BUV, its characteristics must meet the requirements listed in Table 2. These requirements come from the characteristics of the current MAP® ATOX 41-B and from the ECSS-Q-ST-70-02C outgassing standard [1].

Table 2. Requirements for MAP® ATOX 41-B silicone resin

Properties	Requirements
RML (%)	≤ 1
CVCM (%)	< 0.1
Adhesion	0 class

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

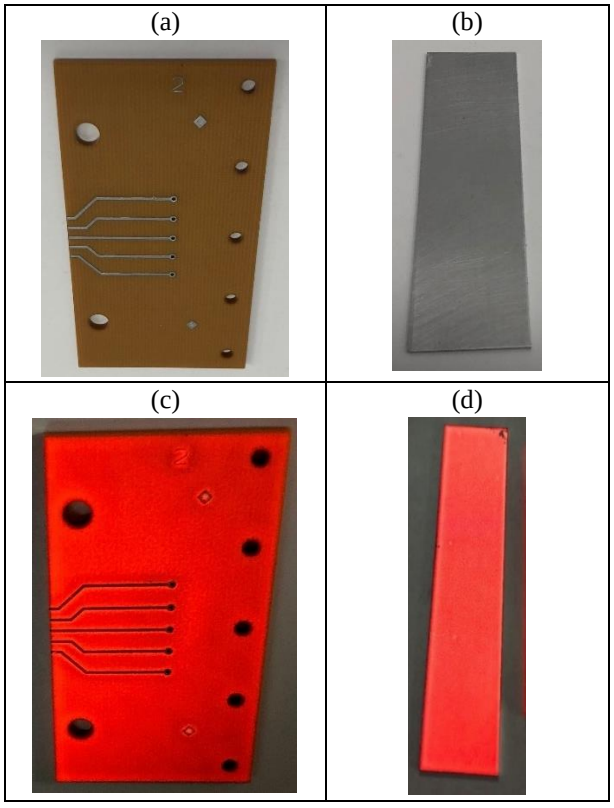
The outgassing properties were measured at the Airbus Toulouse facility on a product after 7 days of curing at 23°C and 55% relative hygrometry. The results are listed in Table 3 [4, 12].

Table 3. Outgassing results for MAP® ATOX 41-B and MAP® ATOX 41-BUV cured for 7 days at 23°C and 55% RH

	TML (%)	RML (%)	CVCM (%)
MAP® ATOX 41-B	0.54	0.52	0.02
MAP® ATOX 41-BUV	0.44	0.39	0.03

MAP® ATOX 41-BUV is transparent when cured (Fig. 2a and b). When using a UV lamp at a wavelength of 254 nm, MAP® ATOX 41-BUV turns red (Fig. 2c and d). The color can vary depending on the substrate.

Figure 2. MAP® ATOX 41-BUV applied to (a, c) Arlon 35N polyimide and to (b, d) 2017-T4 alloy. (a) Arlon 35N polyimide and (b) 2017-T4 alloy under standard light. (c) Arlon 35N polyimide and (d) 2017-T4 alloy illuminated with a UV lamp at 254 nm



4.1.2. RHEOLOGICAL PROPERTIES

The values of the viscosity measurements are listed in Table 4. The viscosity is measured on the MAP® ATOX 41-BUV silicone resin thinned with 75% to 85% MAPSIL® QS thinner. The spraying process parameters are kept the same.

Table 4. Viscosity measurements for MAP® ATOX 41-BUV silicon resin thinned with MAPSIL® QS thinner and comparison with MAP® ATOX 41-B

Properties	MAP® ATOX 41-BUV	MAP® ATOX 41-B
Viscosity – Afnor cup 4 at 23°C (s)	33+/-5	36+/-5

The pot-life was kept at an identical value of 120 minutes at 20°C for MAP® ATOX 41-BUV.

4.1.3. ADHESION

For MAP® ATOX 41-BUV, adhesion was measured following the ISO 2409 standard. The measurements were carried out on aluminum and PCB samples after PSX primer application. The values are 0 class, corresponding to the best ranking of adhesion. These values are the same as those obtained for MAP® ATOX 41-B.

4.1.4. ELECTRICAL PROPERTIES

MAP® ATOX 41-BUV is an electrical insulating material. The electrical properties are listed in Table 5 below [13-15].

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 a statistical treatment of all the values measured.

Table 5. Electrical properties of MAP® ATOX 41-BUV cured for 7 days at 23°C and 55% RH

	MAP® ATOX 41-BUV	MAP® ATOX 41-B
Dielectric strength ($kV.mm^{-1}$)	62.3	72.6
Dielectric constant at 100 Hz	2.1	2.2
Dielectric constant at 100 KHz	3.1	2.1

Dissipation factor at 100 Hz	6.92 x 10^{-4}	3.15 x 10^{-3}
Dissipation factor at 100 KHz	2.47 x 10^{-3}	2.45 x 10^{-3}
Electrical volume resistivity (Ω.cm)	4.48 x 10^{14}	2.38 x 10^{14}
Electrical surface resistance (Ω/□)	2.06 x 10^{15}	2.64 x 10^{14}

4.1.5. THERMAL PROPERTIES

Thermal conductivity was measured according to the flash laser method.
The Cp is 1.52 kJ.kg^{-1}. K^{-1} and the density 1.044 kg.m^{-3}. The thermal diffusivity was 0.098 mm^2.s^{-1}.
Using equation 2, the average thermal diffusivity was 0.16 W.m^{-1}. K^{-1} [16].

The linear coefficient of thermal expansion was measured using TMA [17]. The results are listed in Table 6.

Table 6. Linear coefficient of the thermal expansion of the MAP® ATOX 41-BUV

T (°C)	CTE (10^{-6} K^{-1})
-150 to -120	22
-69 to -52	212
-24 to 255	337

4.2. AFTER AGING TESTS

Aging tests were carried out at the CNES facility for MAP® ATOX 41-BUV. A damp heat test was done at 50°C and 95% RH for 7 days. Additional thermal cycling tests were performed following two steps:

1. Thermal cycling tests in a vacuum. 10 cycles were performed between -170°C and 130°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 -170°C and 130°C with a 10-minute plateau at high and low temperatures (gradient = 5°C/min).

The results are shown in Table 7. The adhesion of the coatings is 0 class on 5 and does not evolve during the aging test.
The recorded temperatures under the thermal vacuum cycles were as follows: -174°C/+132°C. For the thermal cycling at atmospheric pressure, the temperatures were as follows: -179°C/+136°C.

Table 7. Adhesion characteristics of MAP® ATOX 41-BUV in the initial state and after aging tests – MAP® ATOX 41-BUV cured for 7 days at 23°C and 55% RH

MAP® ATOX 41-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 MAP® ATOX 41-B for inspection. In the initial state, all the properties of MAP® ATOX 41-BUV are close to those of MAP® ATOX 41-B. The outgassing properties and adhesion characteristics remained the same for the new version of the MAP® ATOX 41-B.
After aging tests (damp heat test and cumulative thermal cycling), adhesion remained the same.

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 – MAP® ATOX 41-B
4. CNES qualification report, MAP ATOX 41-B with MAPSIL QS thinner, DSO-TB-TH-2020-25110, 2020
5. ISO 2409 standard, Paints and varnishes - cross-cut tests, 2007
6. MAP, Technical data sheet – PSX
7. Arlon 35N technical data sheet
8. ISO 11359-2 standard, 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. ASTM D257-99 standard, Standard Test Methods for DC Resistance or Conductance of Insulating Materials, 2007

11. NF T 30-014 standard, Determination of the flow time of paints, varnishes and similar preparations using French cups, 1983
12. Outgassing report, Airbus PROP-TMCSF-1000210366 – F.13362.O.H, 01 02 2021
13. Measurement of electrical surface resistance and electrical resistivity, LAPLACE report, “2021.04.16_MAP_Resistivite,” 2021
14. Permittivity measurement and dielectric loss factor, LAPLACE report, “2021.04.16_MAP_Spectro,” 2021
15. Dielectric strength measurements in AC 50Hz, LAPLACE report, “2021.04.16_MAP_Rigidite,” 2021
16. Measurement of thermal conductivity, LIMATB report, “Rapport MAP_avril 2021,” 2021
17. Measurement of coefficient of thermal expansion, ELEMCA report, “21T079cR01v1,” 2021