

Development of a Chromium Free Anticorrosion Primer

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Abstract MAPSIL® SILICo has been developed to substitute current chromium-based anticorrosion primers (Sierra, Cr free anticorrosion primers and treatments, 2012; Sierra, MAP management according European regulations for critical substances, 2013). This product complies with following launchers and satellites specifications:

1. Outgassing compliance with the ECSS-Q-70-02C standard for satellite materials (ESA, Thermal vacuum outgassing test for the screening of space materials, 2008);
2. Compliant behaviour towards space environment which includes UV, e⁻, p⁺ and γ irradiations on Earth;
3. Environmental tests behaviour: damp heat test and salt spray test;
4. Good adhesion on aluminum substrates (7075-T0, 6061-T6, 2024-T3) and steel substrates for launcher applications;
5. Compatibility with silicone and polyurethane paints used for satellites (SG121FD, PNC, MAP® AQ PU1...) and launchers (MAP® AQ STATIC, MAPSIL® AS...) (Remaury, White antistatic paint for launcher: MAP® AQ STATIC, CNES report, DCT-TV-TH-NT11-4384, 2011; Remaury, Black polyurethane waterborne non electrically conductive paint: MAP AQ PU1, CNES report, DCT-TV-TH-NT11-3938, 2011; Remaury, White antistatic coating for thermal protection of VEAG and ARIANE 5 launchers: MAPSIL® AS, CNES report, DCT-TV-TH-NT11-5588, 2011).

MAPSIL® SILICo has been developed in accordance with ISO 9001 and EN9100 standards ensuring quality of the products. This product is ITAR and EAR free as it is a co-development of a French company (MAP) and the French Space Agency (CNES).

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Keywords Anticorrosion primer • Launcher • Satellite • MAPSIL® SILICo • MAPSIL® SILICo AS • REACH

Introduction

In order to reduce its impacts on human health and on environment, MAP has decided to develop alternative products to the current ones according to the REACH regulation. As far as the products are concerned, MAP has developed, case by case, since 2008, under CNES Research and Technology contracts, “Chromium free solutions”, as alternative products to chromated primers.

MAPSIL® SILICo has been developed to substitute current chromium-based anticorrosion primers [1, 2]. This product complies with following launchers and satellites specifications:

1. Outgassing compliance with the ECSS-Q-70-02C standard for satellite materials [3];
2. Behaviour towards space environment which includes UV, e[−], p⁺ and γ irradiations on Earth;
3. Environmental tests behaviour: damp heat test and salt spray test;
4. Good adhesion on aluminum substrates (7075-T0, 6061-T6, 2024-T3) and steel substrates for launcher applications;
5. Compatibility with silicone and polyurethane paints used for satellites (SG121FD, PNC, MAP® AQ PU1...) and launchers (MAP® AQ STATIC, MAPSIL® AS...) [4–7].

Moreover, the following specific technical requirements were taken into account:

1. Room temperature curing and heat curing;
2. Only degreasing of the substrates—no use of pickling treatment for instance;
3. Spraying application;
4. Low thickness application, 2–4 μm for satellites and 8–15 μm for launchers applications;
5. Electrical conductivity of the substrate kept in low thickness application.

This paper presents, in the first part, the specifications of the anticorrosion protection for satellite and launchers applications. In the second part, the properties of MAPSIL® SILICo are presented. Finally, the qualification results obtained with MAPSIL® SILICo and MAPSIL® SILICo AS are presented.

Space Industry Requirements

Technical Specifications

As the satellite and launchers can be stored several weeks or months before launching, corrosion phenomena could occur on Earth. In order to prevent satellite parts and launchers from this potential issue, anticorrosion products are used before applying thermal control coatings for satellite and antistatic coatings for launchers.

For instance, on Ariane 5 launcher, polyurethane based antistatic coating MAP AERO STATIC B is applied on metallic and composite parts to provide antistatic protection. Before applying this coating and in order to provide anticorrosion protection MAP AERO WP and MAP AERO P primers are applied.

For satellite, and for the same reason as for launchers, chromated primers such as Phosmap 11 are applied on metallic parts before applying thermal control coatings such as SG121FD, PNC. . . Moreover, most of the aluminium alloys used are treated with Alodine 1200, which is a Cr^{VI} based surface treatment.

Regulatory Specifications

In the European Union, the REACH regulation (Registration, Evaluation, Authorization and restriction of Chemicals) is applicable since 2006. The REACH regulation tends to limit the use of hazardous substances in order to prevent human health and environment. The most critical substances such as Cr^{VI} will require authorization process. Since 2008, taking into account this regulation it has been decided to substitute Cr^{VI} based products. Since this date, most of the alternative products were developed and qualified in 2013. Indeed, the use of these substances will still be authorized until 2018.

MAPSIL® SILICO Specifications for Thin Film Substitution

Typical requirements of anticorrosion products for space uses are based upon (1) damp heat test and (2) salt spray test.

The damp heat test has been done following the ISO 6270 standard [8]. The main parameters of the test were as follows: (1) T = 85 °C, (2) Relative humidity of 95 %, and (3) duration of 14 days. The conformance criteria were the following:

Corrosion: <5 pits for a 130 × 80 mm area;

Electrical resistance: <5 mW following ASTM D257-07 standard [9].

The salt spray test was done following the ISO 9227 NSS [10] and ASTM B117 [11] standards. The main parameters were as follows: (1) $T = 35\text{ }^{\circ}\text{C}$ and (2) NaCl concentration of 5 %. The conformance criteria were the following:

Corrosion: <5 pits for a 130×80 mm area;

Duration: 72 h minimum.

For both tests, the materials used were the aluminium alloys 7075-T0, 6061-T6 and 2024-T3. For the surface preparation we only used a degreasing step with isopropyl alcohol. All the samples were applied using spray gun pulverization with a surface mass of $1.5\text{--}3.0\text{ g m}^{-2}$ resulting in a thickness between 2 and 4 μm .

MAPSIL® SILICO Specifications for Thick Film Substitution

For thick film substitution (launcher uses), only salt spray test is required to evaluate the corrosion resistance. This test has been done following the same standards as previously mentioned. Only the conformance criteria changed, they are defined hereunder:

Corrosion: no damage over 3 mm on both sides of the cut (crossed cut);

Duration: more than 500 h for aluminium alloys and 168 h for steel;

Electrical resistance: no requirement.

The materials tested were the aluminium alloys 7075-T0, 6061-T6 and 2024-T3. The surface preparation consisted in degreasing the surface using isopropyl alcohol. All the samples were applied using spray gun pulverization with a surface mass of $3.0\text{--}6.0\text{ g m}^{-2}$ resulting in a thickness between 8 and 15 μm .

MAPSIL® SILICO Properties

The MAPSIL® SILICO anticorrosion primer is a poly-condensation silicone based product which curing cycle could be either obtained at room temperature ($23\text{ }^{\circ}\text{C}$) or by accelerated heat curing (up to $100\text{ }^{\circ}\text{C}$). The MAPSIL® SILICO is a 2 component product composed of a base and a hardener. The mixing base/hardener weight ratio is 85/15. Standard curing cycle is obtained at room temperature during 48 h. The colour of the base is white, whereas the hardener is translucent. The density of the product is 1.13. Outgassing test has been carried out by INTESPACE laboratory. The RML has been measured at 0.52 % and the CVCM at 0.01 %.

This product is REACH compliant, ITAR and EAR free. Only degreasing of substrates is required. This product is applied by spray gun pulverization.

Table 1 Evolution of electrical surface resistivity versus surface treatment and corresponding thicknesses

Aluminium alloy	Surface treatment	Thickness (μm)	R_s ($\text{k}\Omega/\square$)
7075-T0	MAPSIL® SILICo	2	55
		8	80
2017-T4	Alodine	3	400

MAPSIL SILICO Qualification Results

Satellite Applications

For the anticorrosion evaluation, the results of damp heat test and the salt spray test were compliant: no defects were observed after respectively 14 days and 72 h.

The evolution of electrical surface resistivity versus thickness was also measured. The results are presented in Table 1.

Launchers Applications

The electrical surface resistance of the metallic substrate remains the same using MAPSIL® SILICo, even with thicknesses as thin as 8 μm . On the opposite, with the Alodine 1200 coating, the electrical surface resistance was ten times greater.

MAPSIL® SILICo meets the satellite requirements, therefore it could be an alternative to chromate based conversion coatings such as Alodine 1200. MAPSIL® SILICO has been CNES qualified with MAP® AQ PU1 thermal control coating and with MAPSIL® QS1123 ELEC LD, a silicone adhesive for OSR bonding.

MAPSIL® SILICo Results

For the anticorrosion evaluation, the salt spray test results were compliant, no defects were observed after more than 200 h depending on the substrate nature (Table 2).

Moreover, the MAPSIL® SILICo has been tested and qualified by CNES with both antistatic paints MAP® AQ STATIC and MAPSIL® AS.

Table 2 Duration of the salt spray test depending on the substrate nature

Substrate	Thickness (μm)	Duration (h)
2024-T3	42	>500
7075-T0	10	>1500
Steel	40	>200

Fig. 1 Current whole system for launcher

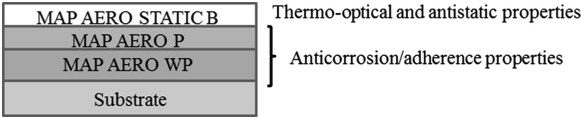


Table 3 Evolution of thermo-optical properties and electrical surface resistance versus thickness

Thickness	22 μm	40 μm	52 μm
α_S	0.46	0.40	0.39
ϵ_{IR}	0.91	0.91	0.91
R_S (MΩ/□)	0.06	0.35	2.00

MAPSIL® SILICO AS Properties

Based upon the MAPSIL® SILICo formulation we have developed the MAPSIL® SILICO AS product which can ensure anticorrosion protection and provide anti-static properties. One product could replace the current whole system used (Fig.1).
To reach a good compromise between thermo-optical properties (α_S and ϵ_R), and antistatic behaviour (R_S), a minimum thickness of 40 μm is required (Table 3).

Conclusions

MAPSIL® SILICo was developed to provide a Chromium free, corrosion protection for light aluminum alloys and to be covered by thermal control coatings and antistatic paints. For launcher use, MAPSIL® SILICo applied as a thick layer (8–15 μm) provides a good corrosion resistance on aluminum alloys and steel. For satellite use and Alodine 1200 substitution, applied as a 2–4 μm thick layer MAPSIL® SILICo provides anticorrosion protection and electrical conductivity. This product has been already qualified by CNES with white antistatic coatings for launchers and thermal control coatings for satellites.
MAPSIL® SILICo AS has been developed for launcher use, to provide anticorrosion protection, antistatic and thermo-optical properties, to replace the current whole system (MAP AERO WP + MAP AERO P + MAP AERO STATIC B)

References

1. Sierra G (2012) Cr free anticorrosion primers and treatments. In: 3rd electronic materials and assembly processes for space, workshop, Genoa, Italy
2. Sierra G (2013) MAP management according European regulations for critical substances. In: NASA international workshop on environment and alternative energy 2013, Frascati, Italy
3. ESA (2008) Thermal vacuum outgassing test for the screening of space materials
4. Remaury S (2011) White antistatic paint for launcher: MAP® AQ STATIC, CNES report, DCT-TV-TH-NT11-4384
5. Remaury S (2011) Black polyurethane waterborne non electrically conductive paint: MAP AQ PU1, CNES report, DCT-TV-TH-NT11-3938
6. Remaury S (2011) White antistatic coating for thermal protection of VEAG and ARIANE 5 launchers: MAPSIL® AS, CNES report, DCT-TV-TH-NT11-5588
7. Remaury S (2013) Qualification of MAPSIL® QS1123 ELEC LD adhesive, CNES report, DCT-TV-TH 2013-2456
8. ISO 6270-2: 2005 standard, Paints and varnishes – determination of resistance to humidity
9. ASTM D257-07, Standard test methods for DC resistance or conductance of insulating materials
10. ISO 9227 NSS, 2006-07-15, Corrosion tests in artificial atmospheres – salt spray tests
11. ASTM B117-16, Book a standards 03. 02, Standard practice for operating salt spray (Fog) apparatus

<http://www.springer.com/978-3-319-19308-3>

Protection of Materials and Structures from the Space
Environment

ICPMSE-11

Kleiman, J. (Ed.)

2017, XVI, 603 p. 403 illus., 289 illus. in color.,

Hardcover

ISBN: 978-3-319-19308-3