EVALUATION OF A NEW STRONTIUM CHROMATE FOR THE FORMULATION OF PRIMERS USED IN SPACE APPLICATIONS

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ABSTRACT

Due to REACH environmental regulation, chromate compounds are meant to be banned for the industrial use from January 2019. Nevertheless, as REACH allows authorization process, some companies have built an authorization dossier for a specific strontium chromate. In order to check the ability to use such reference in our existing primers PHOSMAP 11, MAP AERO P and MAP AERO WP, validation tests were carried out.

These tests were defined on the basis of the production controls used up to now with the current products. These tests include rheological measurement (viscosity and pot-life), thickness and adhesion. Then, in a second step, the most stringent tests of the initial qualification were carried out. For satellite application, the thermal cycling test under vacuum was carried out, whereas for launcher products, the tests were the following: cold test, dry heat test, rain test, accelerated ageing test, salt spray test and thermal shock test.

All the properties that were controlled at the initial state and then after the ageing tests that were performed during the qualification phase met the requirements and were identical to the current products PHOSMAP 11, MAP AERO P and MAP AERO WP.

1. INTRODUCTION

REACH, which stands for Registration, Evaluation, Authorisation and Restriction of Chemicals, is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry. Ethical and economic objectives are thus put forward and intertwined within this regulation; they follow the often called 'No data, no market' line [1].

Special attention is given to chemicals classified as carcinogenic, mutagenic or reprotoxic (CMR). A second central plank of REACH is the principle of substitution: if safer alternatives exist, certain dangerous substances – the 'Substances of Very High Concern' (SVHC) – must be phased out. Whereas previously chemicals could only be banned if proven to be dangerous, REACH requires EU industry and importers to prove that each substance intended for the market is safe for human health and the environment.

As stated by REACH, the chromates compounds which are CMR will be forbidden from January 2019. In order to prevent any interruption of production and to ensure its customers the continuous procurement of its coatings, MAP has taken this opportunity to develop and to propose innovative REACH compliant products for the space sector [2,3].

Nevertheless, as allowed by REACH, an authorization dossier has been built for the chromate, due to the difficulty in finding any substitution for such components. The authorization of the use of some strontium chromates will probably last until 2031. Taking this opportunity, MAP has developed a specific program which aims to use this specific raw material in substitution of current chromates used up to now in the following products targeted by REACH: PHOSMAP 11, MAP AERO P and MAP AERO WP products. This specific raw material will be called "authorized strontium chromate" hereafter.

PHOSMAP 11 is a wash primer which is mainly used for satellite applications. This primer guarantees good adhesion on most of the substrates used in this activity field, such as Aluminium alloys treated with Surtec 650, silver or gold, TA6V, INVAR, Stainless steel…

MAP AERO P and MAP AERO WP are corrosion protection primers used for launcher applications. These products have been qualified since the use of Ariane 4 in 1986.

In order to check the ability of the new chromate to replace chromates used in these 3 above mentioned products, we have defined the following qualification plan:

1. Control of the product at initial stage;
2. Application and ageing tests.

First, this paper presents the properties of the current products. Second, these properties are compared with those of the products manufactured from the "new chromate" and then, third, the ageing tests are presented.

2. MATERIALS, PROCESSES AND TECHNIQUES

2.1. Materials

Since its creation in 1986, MAP has developed numerous products for the space industry. From these products, the following primers PHOSMAP 11, MAP AERO P and MAP AERO WP are subjected to REACH regulation. The main properties of these primers are listed in Tab.1.

Table 1. General properties of the PHOSMAP 11, MAP AERO P and MAP AERO WP primers

	Phosmap 11	MAP AERO WP	MAP AERO P
Solvent	Organic	Organic	Organic
Solid contents mix (%)	15.3	15.3	70
VOC rate (g/L)	791	778	603
Thickness (µm)	5 - 10	8 - 10	20 – 30
Consumption (g/m^2/ dry µm)	1.7	1.5	2.0
Mixing weight ratio	50 / 50	50 / 50	83 / 17
Pot Life at 20°C (h)	8	8	8
Viscosity of the mix (s) with Afnor cup N°4	14 - 18	14 - 18	14 - 18

The chromates used up to now for the production of these products are listed in Tab.2.

Table 2. Presentation of the chromates used in the three primers PHOSMAP 11, MAP AERO P and MAP AERO WP

	CAS	Phosmap 11	MAP AERO WP	MAP AERO P
Strontium chromate	7789-06-2			X
Zinc tetraoxychromate	49663-84-5		X	
Zinc and potassium chromate	11103-86-9	X		

As all the chromates used into the formulation of the primers are listed on the ANNEX XIV of REACH 1907/2006 REACH regulation, the sunset date has been defined to the 22nd January 2019. After the sunset date, the purchasing and use will be forbidden except for the raw materials that have been registered and for which an authorization dossier has been built. The authorized strontium chromate has been registered by several manufacturers and end-users. For this reason MAP has decided to evaluate the formulation of all three primers from this new chromate. The main characteristics of all the chromates used are listed in Tab.3. The data are issued from the technical data sheets of the raw materials.

Table 3. Main characteristics of the chromates used and the substitute

	CAS	Oil absorption (g/100 g)	Density
Strontium chromate	7789-06-2	24 ± -4	3.9
Zinc tetraoxychromate	49663-84-5	35 ± 5	3.6
Zinc and potassium chromate	11103-86-9	25	3.4
Authorized strontium chromate	7789-06-2	24	3.9

2.2. Processes

The primers and the top-coat were applied according to the technical data sheets [4-7].
Primers were applied using a Kremlin S3 spray gun.

2.2.1. Initial control

The primers were applied on 2017-T4 alloy, for the initial control, following the production control sheet. The curing conditions were as followed.

Table 4. Curing conditions for PHOSMAP 11 and MAP AERO WP primers

	Phosmap 11	MAP AERO WP
Temperature (°C)	23	23
Hygrometry (%)	55	55
Time (h)	8	2

Table 5. Curing conditions for MAP AERO P primer

	1st step	2nd step
Temperature (°C)	23	80
Hygrometry (%)	55	-
Time (h)	8	16

2.2.2. Ageing tests

2.2.2.1. Launcher products

MAP AERO P and MAP AERO WP primers are not used alone; they are used with a top-coat. The ageing tests were then performed in an industrial configuration which is the following:

- MAP AERO WP + MAP AERO P + MAP AERO STATIC B [11]

The system has been applied on 7075-T0 alloy, which dimensions were as followed: 80 mm x 80 mm x 1 mm.

The MAP AERO WP and MAP AERO P are cured at room temperature (23°C and 55% HR). A covering time of 2 h is used between both primers and between MAP AERO WP and MAP AERO STATIC B.
The final curing of the system is described in Tab.6

Table 6. Curing conditions for MAP AERO STATIC B

	1st step	2nd step
Temperature (°C)	23	80
Hygrometry (%)	55	-
Time (h)	8	16

2.2.2.2. Satellite products

Phosmap 11 is a corrosion protection primer, it is not applied alone. The main top-coats used with this primer are PU1 [8] and PUK [9] paints.

The ageing tests were based upon the qualification performed for Phosmap 11 + PU1 and Phosmap 11 + PUK [10,11].

The main substrates used for satellites applications are the following:

- 2017-T4 ;
- Al-Ag ;
- Al-Au ;
- TA6V (PU1) ;
- INVAR (PU1).

2.3. Techniques

At the initial state, the viscosity of the product is measured using Afnor Cup following the ISO 2431 standard [12].

Once applied, the following properties were checked:

- Thickness measurement [13];
- Adhesion test [14];
- R_S measurement [15];
- Alpha measurement [16].

3. QUALIFICATION PLAN

3.1. Launcher products

Based upon the general qualification plan for the launcher products [17-19], we have selected the most critical tests listed hereunder with a brief description.

3.1.1. Cold test

This test consists in applying a temperature of -30 ± 2°C to the material for a length of time equal to or greater than 5 h. The temperature increase/decrease rate is defined at 2°C/min. This test was performed in a climatic chamber (ESPEC PSL 2KTH) under atmospheric air for 6h.

3.1.2. Dry heat test

This test consists in applying a temperature of 70 ± 2°C to the material for a length of time equal to or greater

than 5h, with less than 50% humidity at 35°C. The temperature increase/decrease rate is defined at 2°C/min. This test was performed in a climatic chamber (ESPEC PSL 2KTH) under atmospheric air for 6h.

3.1.3. Rain test

This test consists in watering the entire surface of the material continuously and regularly for a given time, respecting the intensity and the temperature of the water spray. In our case, time was set at 30 min at an intensity of 480 l/h at 19°C (24 mm/cm^2).

3.1.4. Accelerated ageing test

This test combines a damp heat test and temperature cycling at atmospheric pressure, under atmospheric air flushing.
Cycle 1: 5 days at 80°C and 95% RH + 10 cycles from -10°C to 50°C (with stages of 1h30 and a gradient of 2°C/min).
Cycle 2: 5 days at 50°C and 95% RH + 10 cycles from -10°C to 50°C (with stages of 1h30 and a gradient of 2°C/min).
Damp heat testing and temperature cycling were performed in a climatic chamber (ESPEC PSL 2KTH).

3.1.5. Salt spray test

This test consists in spraying the material with a saline solution with a mass composition of NaCl 5% + H_2O 95 % at pH 7 at 35°C. Two cycles were performed, 24 h with salt spray and 24 h without spray. The specific chamber used is referenced ASCOTT S120T.

3.1.6. Thermal shock test

This test consists in rapidly transferring the material from room temperature (stabilized) to liquid nitrogen temperature at which it is then maintained for 10 min. Controls were carried out after the nitrogen had completely evaporated.

3.2. Satellite products

Based upon the general qualification plan for the satellite products [10,11], we performed thermal cycling test à ambient pressure between -170°C and 130°C. 100 cycles were performed.

In order to qualify paints for space use, adhesion must be validated after thermal cycling tests under vacuum. These tests were carried out within CNES facilities under the following experimental conditions:

- Vacuum: 10^{-6} Torr
- Hot/cold stage duration: 15 minutes
- Temperature slope: 10°C/min
- Number of cycles: 100

Thermal cycling tests have been carried out on five industrial substrates:

- 2017-T4 aluminium
- Silver coated aluminium
- Gold coated aluminium
- INVAR
- TA6V

The minimal and maximal measured temperatures were respectively of -170°C and 132°C on metallic substrates.

4. RESULTS

4.1. Launcher products

The initial controls performed on MAP AERO WP with the new chromates are listed in the table below. All the measured values were in the requirement range.

Table 7. Initial control performed on MAP AERO WP

Properties	Requirement	Value
Base viscosity (s) Afnor cup N°6	40 ± 10	47
Mix viscosity (s) Afnor cup N°4 (t0)	16 ± 2	17.4
Mix viscosity (s) Afnor cup N°4 (t0 + 8h)	≤ 32 ± 4	17.5
Thickness (µm)	8 - 10	9
Adhesion	0 Class	0

The initial controls performed on MAP AERO P with the new chromates are listed in the Tab.8. All the measured values were in the requirement range.

Table 8. Initial control performed on MAP AERO P

Properties	Requirement	Value
Base viscosity (s) Afnor cup N°6	30 ± 10	37.4
Mix viscosity (s) Afnor cup N°4 (t0)	16 ± 2	16.1
Mix viscosity (s) Afnor cup N°4 (t0 + 8h)	≤ 32 ± 4	21.5
Thickness (µm)	20 - 30	28
Adhesion	Classe 0	0

In a second step, ageing tests were performed on the following system which includes MAP AERO WP + MAP AERO P + MAP AERO STATIC B. The results are mentioned in Tab.9.

Table 9. Results after ageing tests - MAP AERO WP + MAP AERO P + MAP AERO STATIC B applied on 7075-T0 alloy (system1)

Tests	Adhesion (Class)	Rs (MΩ/□)	α
Requirement	0	1 to 100	0.43 ± 0.02
t0	0	5.5	0.45
Cold test	0	6.4	0.44
Dry heat test	0	5.4	0.45
Rain test	0	6.1	0.45
Accelerated ageing test	0	1.2	0.43
Salt spray test	0	2.6	0.45
Thermal shock test	0	6.0	0.45

All the properties after each ageing met the requirement.

4.2. Satellite products

The initial controls performed on PHOSMAP 11 formulated with the new chromates are listed in the table below. All the measured values met the requirement.

Table 10. Initial control performed on PHOSMAP 11

Properties	Requirement	Value
Base viscosity (s) Afnor cup N°6	60 ± 15	55.8
Mix viscosity (s) Afnor cup N°4 (t0)	17 ± 1	17.9
Mix viscosity (s) Afnor cup N°4 (t0 + 8h)	≤ 32 ± 4	17.5
Thickness (µm)	5 - 10	6
Adhesion	Classe 0	0

In a second step, ageing tests were performed on the following systems:

- PHOSMAP 11 + PUK
- PHOSMAP 11 + PU1

The substrates that were used are listed in Table 11.

Table 11. Adhesion tests results after ageing tests – PHOSMAP 11 + PUK

Adhesion (Class)	Initial state	After thermal cycles
A 2017 T4	0	0
Silver coated Al	0	0
Gold coated Al	0	0

Table 12. Adhesion tests results after ageing tests – PHOSMAP 11 + PU1

Adhesion (Class)	Initial state	After thermal cycles
A 2017 T4	0	0
INVAR	0	0
TA6V	0	0

5. CONCLUSION

The use of the authorized strontium chromate in substitution of the current chromates, strontium chromate, Zinc tetraoxychromate Zinc and potassium chromate in PHOSMAP 11, MAP AERO P and MAP AERO WP primers has been done.

The characterization tests performed at the initial state (viscosity, pot-life, thickness and adhesion) were all compliant.

The ageing tests defined from the initial qualification of the products were successfully carried out. All the properties checked at the initial state and after ageing tests performed during qualification phase met the requirement and are identical to the current products PHOSMAP 11, MAP AERO P and MAP AERO WP.

6. REFERENCES

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