ANALYSIS OF ALTERNATIVES

Legal name of applicants:	*AKZO Nobel Car Refinishes B.V.* *Habich GmbH;* *Henkel Global Supply Chain B.V.;* *Indestructible Paint Ltd.;* *Finalin GmbH;* *Mapaero;* *PPG Central (UK) Ltd in its legal capacity as Only Representative of PRC DeSoto International Inc. - OR5;* *PPG Industries (UK) Ltd;* *PPG Coatings SA;* *Aviall Services Inc.*
Submitted by:	*AKZO Nobel Car Refinishes B.V.*
Substance:	*Strontium chromate, EC No: 232-142-6, CAS No: 7789-06-2*
Use title:	*Application of paints, primers and specialty coatings containing Strontium chromate in the construction of aerospace and aeronautical parts, including aeroplanes / helicopters, space craft, satellites, launchers, engines, and for the maintenance of such constructions, as well as for such aerospace and aeronautical parts, used elsewhere, where the supply chain and exposure scenarios are identical.*
Use number:	*2*

Disclaimer

CONTENTS

List of Figures:

List of Tables

Abbreviations

AA2024	Aluminium alloy, most commonly used in the aerospace sector
ACF	Airbus Chromate-Free
Al	Aluminium
Acute Tox.	Acute Toxicity
AIE	Alternate Immersion Test
AMMTIAC	Advanced Materials, Manufacturing, and Testing Information Analysis Center
AoA	Analysis of Alternatives
Asp. Tox.	Aspiration hazard
ASTM	American Society for Testing Materials
Aquatic Acute	Hazardous to the aquatic environment
Aquatic chronic	Hazardous to the aquatic environment
BSA	Boric-Sulphuric Acid Anodizing
BZT	Benzotriazoles
CAA	Chromic Acid Anodizing
Carc.	Carcinogenicity
CAS	unique numerical identifier assigned by Chemical Abstracts Service (CAS number)
CCC	Chemical Conversion Coatings
CCST	Miscellaneous Chromium VI Compounds for Surface Treatment REACH Authorization Consortium
Cd	Cadmium
CPVC	Critical Pigment Volume Concentration
Cr	Chromium
Cr(0)	Elementary Chromium
Cr(III)	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
CRES	Corrosion resistant steel
CSR	Chemical Safety Report
DoD	Department of Defense
DT&E	Development, Test and Evaluation
EASA	European Aviation Safety Agency

EC	unique numerical identifier of the European Community (EC number)
EHS	Environmental Health and Safety
EMI	Electromagnetic Interference
EN	European Norm
EPA	Environmental Protection Agency
ESA	European Space Agency
EU	European Union
Eye Dam.	Serious ey damage
Eye Irrit.	Eye irritation
Flam. Liq.	Flammable liquid
Flam.sol.	Flammable solid
HITEA	Highly Innovative Technology Enablers for Aerospace
HVOF	High Velocity Oxy Fuel
ISO	International Organization for Standardization
Me	Metal
Met. Corr.	Substance or mixture corrosive to metals
Mg	Magnesium
Mil-DTL	United States Military Standard
MoCC	Molybdate-based conversion coatings
MRL	Manufacturing Readiness Level
MRO	Maintenance, Repair and Operations
SDS	Safety Data Sheet
Muta.	Germ cell mutagenicity
NASA	National Aeronautics and Space Administration
NDSU	North Dakota State University
Ni	Nickel
OEM	Original Equipment Manufacturer
OT&E	Operational Test and Evaluation
Ox. Sol.	Oxidising solid
Pr	Praseodymium
Press. Gas	Gases under pressure
PSA	Phosphoric Sulphuric Acid Anodizing

PU	Polyurethane
PVC	Pigment Volume Concentration
Pyr. Liq.	Pyrophoric liquid
Pyr. Sol.	Pyrophoric solid
QPL	Qualified Products List
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
R&D	Research and Development
Repr.	Reproductive toxicity
Resp. Sens.	Respiratory
RoHS	Directive on Restriction of Hazardous Substances
ROPCAS	Research of organic primer concepts for aluminium substrates
SEA	Socio Economic Analysis
Skin. corr.	Skin corrosion
Skin. Sens.	Skin sensitisation
Skin irrit.	Skin irritation
SST	Salt spray test
(S)TC	(Supplemental) Type Certificate
STOT RE	Specific target organ toxicity, repeated exposure
STOT SE	Specific target organ toxicity, single exposure
SVHC	Substance of Very High Concern
TC	Type Certificate
Ti	Titanium
TRL	Technology Readiness Level
TSA	Tartaric-Sulphuric Acid Anodizing
US	United States
VOC	Volatile Organic Compounds
VTMS	Vinyl trimethoxysilane

Glossary

Term	Definition
Active corrosion inhibition	The ability of a material to spontaneously repair small amounts of chemical or mechanical damage that exposes areas of metal without any surface protection (“self-healing properties”). This functionality is advantageous and enhances service life duration of parts, maintenance intervals and on-flight security of air travellers.
Adhesion promotion	Parameter describes the tendency of dissimilar particles or surfaces to cling to one another (for example adhesion of coating to substrate, adhesion of paint to coating and/or substrate).
Aerospace	This terms comprises civil and military applications of aviation and space industry.
Aeronautics	This term comprises the study of the science of navigation through air and space. It defines the methodology of how to design an aircraft, spacecraft or other flying machine.
Alternative	Candidate alternative that has been tested, qualified, fully industrialised and certified by the Aerospace OEM. The definition is only used for the final classification of evaluated alternatives.
Basic primer	Basic primers represent the largest volume primer coating due to their universal applicability to many substrates and compatibility with many subsequent coatings. Chromated basic primers are used since decades to coat metallic parts. Basic primers or paint primers are also sometimes called “green primers” because the usual colour is green. Their main purpose is corrosion protection although they must simultaneously provide good adhesion between the metal surface and further coating layers. Basic primers must be compatible with any subsequent layer applied to it. Basic primers are applied as basic layer of a multi-layer paint or coating system
Bath	Typical method for surface treatment of parts. May also be referred to as dipping or immersion. None-bath methods include wiping, spraying, and pen application.
Bonding	The process where two parts are joint together by means of a bonding material; an adhesive sometimes in combination with a bonding primer and a conversion or anodizing treatment
Bonding primer	Adhesive bonding involves joining together two or more metal or nonmetal components. This process is typically performed when the joints being formed are essential to the structural integrity of the aerospace vehicle or component.
Candidate Alternative	Potential alternative provided to the Aerospace OEM for their evaluation. These have already been evaluated in the labs of formulators.
Certification	Verification that an aircraft and every part of it complies with all applicable airworthiness regulations and associated Certification Specifications (specs).
Chemical resistance	Parameter is defined as the ability of solid materials to resist damage by chemical exposure.
Civil and military applications	The flight profile in civil aviation is limited to ferrying passengers and cargo, while in military applications several missions have to be taken into account that require constant technical trade-offs. The flight frequency of military planes is very low compared to civil planes running on a daily basis. Based on these daily demands to ensure the airworthiness of civil

Term	Definition
	aircraft, the requirements are much more comprehensive. As both applications follow closely the same development and approval process as indicated in chapter 5, they are covered within this dossier.
Coating	A coating is a covering that is applied to the surface of an object, usually referred to as the substrate. The purpose of applying the coating may be decorative, functional, or both. A coating may be organic (e.g. primer, topcoat or specialty coating, or inorganic (e.g. hard chrome, cadmium or zinc-nickel plating, thermal spray, anodize).
Commercial exterior aerodynamic structure primer	An example of a specialty coating. Commercial exterior aerodynamic structure primer means a primer used on aerodynamic components and structures that protrude from the fuselage, such as wings and attached components, control surfaces, horizontal stabilizers, vertical fins, wing-to-body fairings, antennae, and landing gear and doors, for the purpose of extended corrosion protection and enhanced adhesion.
Compatibility (with substrate/or other coatings)	The capability of two or more things to exist or perform together in combination without problems or conflict. In this document context usually refers to substrate, coatings or other materials and fluids
Corrosion inhibitor	Compound of a primer/paint formulation providing corrosion protection. Corrosion inhibitors can be categorised according to basic quality criteria including inhibitive efficiency and versatility, toxicity, and price. Ideally, the corrosion inhibitor is compatible with all primer, paint, and specialty coating systems and performs effectively on all typical metal substrates. Furthermore it has to guarantee product stability (chemically, thermally, and regarding particle size distribution), reinforce the useful coating properties and needs to have reasonable rheological behaviour in the paint /primer formulation.
Corrosion protection	Means applied to the metal surface to prevent or interrupt oxidation of the metal part leading to loss of material. This can be a metal conversion coating or anodizing, a pre-treatment, paint, water repellent coating, liquid, adhesive or bonding material.sea
Corrosion resistance	The ability of a metal aircraft part to withstand gradual destruction by chemical reaction with its environment.
Counterpart	Structural zone (like assembly, component) to which a given assembly/part is fitted.
Fuel tank primer	Fuel tank coating means a coating applied to fuel tank components for the purpose of corrosion and/or microbial growth inhibition and to assure sealant adhesion in extreme environmental conditions.
Implementation	After having passed qualification and certification, the third step is to implement or industrialise the qualified material or process in all relevant activities and operations of production, maintenance and the supply chain.
In-service evaluation	In-service evaluations are common practice to validate accelerated corrosion results obtained in the laboratory to determine correlation between accelerated corrosion testing and when used on operating aircraft.
Key Functionalities	Have been identified during the consultation phase for all parts of the process chain and are used for the evaluation of alternatives.
Legacy Part	A legacy part shall mean any part of an end product for aerospace which is manufactured in accordance with a type certification applied for before the earliest sunset date (including any further supplemental or amended type certificates or a derivative) **or** for defence and space which is designed in

Term	**Definition**
	accordance with a military or space development contract signed before the earliest sunset date, and including all production, follow-on development, derivative and modification program contracts, based on that military or space development program.
Materials control	Portion of a specification that controls which materials may be used in the process. Products that have met all requirements may be added to this list by the OEM.
Primer	Primer means the first layer and any subsequent layers of identically formulated coating applied to the surface of an aerospace vehicle or component. Primers are typically used for corrosion prevention, protection from the environment, functional fluid resistance, and adhesion of subsequent coatings. Primers that are defined as specialty coatings are not included under this definition.
Processing temperatures	Ability to be processed/ implemented at the specific temperature of the respective use/process.
Qualification	OEM validation and verification that all material, components, equipment or processes have to meet or exceed the specific performance requirements which are defined in the Certification Specifications documented in technical standards or specifications.
Qualified product list	A document related to a specification that controls which materials may be used in the process. Products that have met all requirements may be added to this list by the OEM.
Risk reduction	Classification and labelling information of substances and products reported during the consultation being used for alternatives / alternative processes are compared to the hazard profile of the used chromate.
Specialty coating	A specialty coating (or speciality coating) is a coating that, even though it meets the definition of a primer, topcoat, or self-priming topcoat, has additional performance criteria beyond those of primers, topcoats, and self-priming topcoats for specific applications.
Temperature resistance (Thermal shock resistance)	The ability of a material, in this context mostly referring to coatings, primers and paints, to withstand repeated low and high temperature cycling.

1. SUMMARY

This application for Authorisation (AfA) is the culmination of extraordinary effort across industry over several years to share data and prepare a comprehensive and reliable assessment of alternatives that is representative for the industry.

The aerospace industry recognises that the use of such sector-specific approach in an upstream application will facilitate assessment by the SEAC. Without this approach, multiple applications for authorisation utilising different approaches, assumptions and terminology are unavoidable; such differences could present challenges for enforcement across the industry.

The Analysis of Alternatives (AoA) is based on extensive input and data held by the aerospace sector, associated industries and third parties. The same companies and facilities have reviewed and validated the findings in detail and agree that the AoA is representative of the situation across the industry.

This AoA forms part of the AfA for the use of strontium chromate in the application of paints, primers, and specialty coatings (hereafter ‘coatings’) in the aerospace and aeronautics sectors.

A coating is a material that is applied to the surface of a part to form a protective, functional or decorative solid film. Protective coatings containing strontium chromate in concentrations generally between 1 and 25% w/w are used in the production and repair of aeroplanes, helicopters, spacecraft, satellites, launchers and engines, as well as their component parts. The coatings are generally applied in an industrial setting by spray, brush or roller application. Approximately 200 tonnes of the strontium chromate are used in such coating applications within the scope of this AfA per year.

Strontium chromate functions as an effective corrosion prevention and inhibiting agent in coatings that can be applied to lightweight metals and alloys, including aluminium, magnesium, steel and titanium. For this reason, coatings that meet specific corrosion performance requirements often contain strontium chromate and are specified as part of, and fundamental to the effectiveness of, corrosion prevention and retardation systems within the aeronautics and aerospace industries, which use all these metals in the manufacture of aircraft and spacecraft. The very low solubility of strontium chromate makes it suitable for the use in these coating systems which must provide a reliable and durable coating and/or seal.

This summary aims to shortly explain why use of strontium chromate in coatings is essential to the aerospace and aeronautics sector. It describes the steps and effort involved in finding and approving a replacement for strontium chromate in these applications and evaluates potential alternatives in detail (chapter 6 and 7).

Background to strontium chromate-based coatings

Chromates have been used for more than 50 years to provide corrosion protection to critical components and products within the aerospace sector, where the products to which they are applied must operate to the highest safety standards in highly demanding environments for extended time periods. Coatings based on strontium chromate have unique technical functions that confer substantial advantage over potential alternatives. These include:

- Outstanding corrosion protection and prevention for nearly all corrosion sensitive metals under a wide range of conditions
- Active corrosion inhibition (self-sealing, e.g. repairing a local scratch to the surface)
- Excellent adhesion properties to support application to the substrate and subsequent coating layers

Use of strontium chromate in surface treatment for the aerospace sector

Cr(VI)-based coatings are specified in the aerospace sector primarily because they provide superior corrosion resistance and inhibition (see Chapter 3.4). These characteristics and the quality of the product are essential to the safe operation and reliability (airworthiness) of aircraft and spacecraft which operate under extreme environmental conditions. These structures are extremely complex in design, containing millions of highly specified parts, many of which cannot be easily inspected, repaired or removed. Structural components (e.g. landing gear, fasteners) and engine parts on aircraft are particularly vulnerable to corrosion.

The complexity of aircraft or spacecraft construction and range of environmental conditions that aircraft must withstand makes corrosion prevention a very challenging task. In practice, multiple coatings, such as pre-treatments[1], primers (non-specialised and specialised), and top coats including paints (see **Figure 1** and **Table 1**) are specified to achieve the strict performance requirements necessary for regulatory compliance and for public safety in these sectors, as described further below and in Chapter 5. Each coating type and material is different because it must meet individual functionalities and performance standards particular to a specific design.

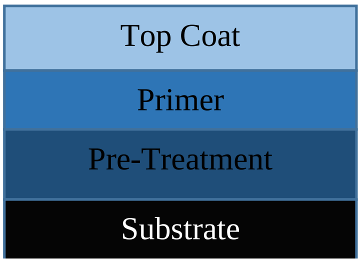

Figure 1: Example of multi-layered coating

In general, strontium chromate-based coatings are specified as one element of a complex system with integrated, often critical performance criteria. Compatibility with and technical performance of the overall system are primary considerations of fundamental importance during material specification.

Table 1: Overview of key requirements for corrosion-resistant coatings

Type of Coating	Description of Coating	Critical Functionality of Coating
Primer and Basic Primer (non-specialised primer)	Corrosion-inhibiting coating applied as first complete coat.	• Corrosion-inhibition • Adhesion to both substrate and subsequent layers • Compatibility with subsequent layer
Bonding primer (specialised primer)	Adhesive bonding involves joining together two or more metal or nonmetal components and protection against corrosion where structural integrity is essential to the aerospace vehicle or component.	• Corrosion-inhibition • Adhesion to both substrate and subsequent layers • Compatibility with subsequent layer

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[1] This use is the subject of a separate Application for Authorisation, due to critical differences in Exposure Scenario and supply chain between coatings and surface treatments

Commercial Exterior Aerodynamic Structure Primer (specialised primer)	Use on aerodynamic components and structures protruding from the fuselage (e.g. wings, landing gear).	• Corrosion-inhibition • Adhesion to both substrate and subsequent layers

This means that, while the use of strontium chromate (or a similar chromate) may be specified at different points in a coating system, it cannot be entirely replaced without impacting the technical performance of the final article. The implications of this are important as Cr(VI)-free alternatives for some individual coating products are available and used by industry. However, where this is the case, chromates are always specified elsewhere in the system. Following years of research and development, coating systems have been developed to substitute chromates in some parts of some coating systems for which corrosion-prevention is a critical parameter; however, such coating systems still incorporate at least one layer (most often the primer or a pre-treatment layer) of chromate-based coating. No complete Cr(VI)-free coating system, providing all the required properties to the surfaces of all articles in the scope of this application, is available. Complete coating systems that do not contain any Cr(VI) substances are only in early evaluation stages at this time. **Figure 2** provides an overview of the development of potential alternatives to Cr(VI)-based coating systems to date, and aims for the future, assuming ongoing programs are successful.

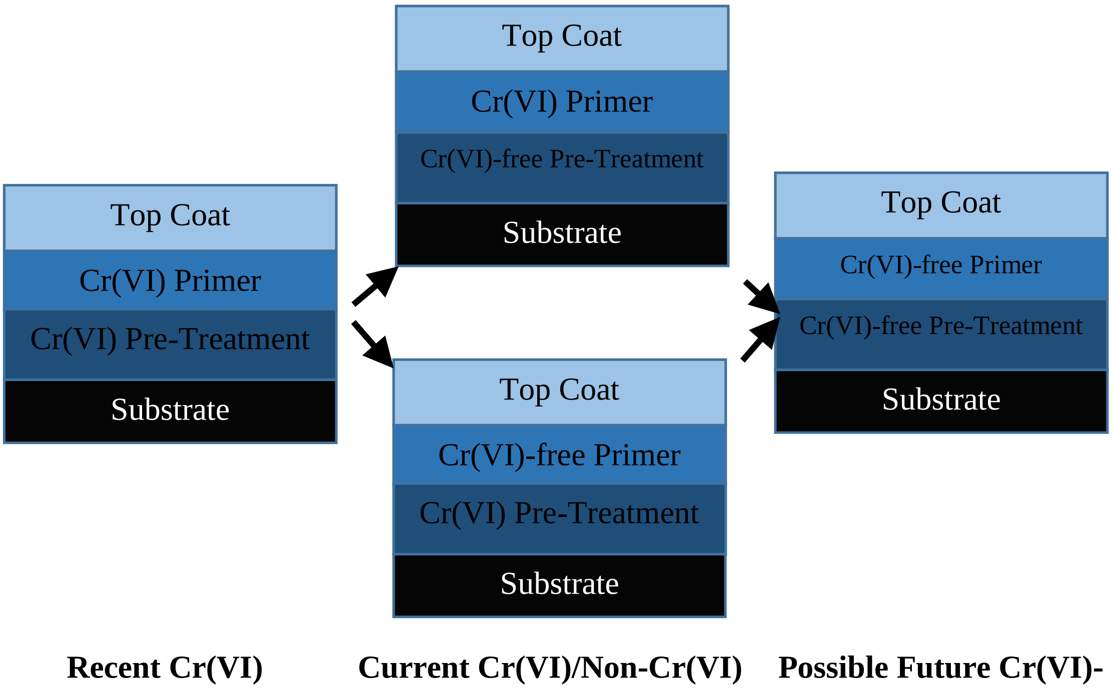


Figure 2: Development of corrosion-prevention coating systems, from past to future (AMMTIAC, 2012, amended)

It is therefore imperative to consider the surface treatment system as a whole, rather than the step involving strontium chromate on its own, when considering alternatives for such surface treatment systems.

Chromate coatings have been successively refined and improved as a result of many decades of research and experience in the sector, and reliable data is available to support their performance. While corrosion cannot be totally prevented, despite the highly advanced nature of Cr(VI)-based coating systems in place today, there is also extensive experience, amassed over decades, on the appearance and impact of corrosion to support its effective management in these systems. On the other hand, while several potential alternatives to strontium chromate-based primers, paints and specialty coatings (see **Table 2**) are being investigated, results so far do not support reliable conclusions regarding their performance in demanding environments and real-world situations. These potential alternatives do not support all the properties of Cr(VI)-based coatings and their long-term performance can currently only be estimated. Decreased corrosion protection performance would necessitate shorter inspection intervals, with a substantial impact on associated maintenance costs.

Identification and evaluation of potential alternatives for the aerospace sector

An extensive literature survey and consultation with aerospace industry experts was carried out to identify and evaluate potential alternatives to strontium chromate. Over 50 potential alternatives were identified. 11 potential or candidate alternatives (including processes and substances) are a focus for ongoing research and development (R&D) programs and are examined in further detail in this report. Here, a candidate alternative is defined as a potential alternative provided to the aerospace manufacturer for evaluation following initial evaluation by the formulator. **Table 2** at the end of this section summarises the main findings of the AoA for the aerospace sector. In Figure 4, the development status of the alternatives is illustrated.

In summary, the analysis shows there are no technically feasible alternatives to strontium chromate-based coating systems for key applications in the aerospace sector. Several potential alternatives are subject to ongoing R&D, but do not currently support the necessary combination of key functionalities to be considered technically feasible alternatives.

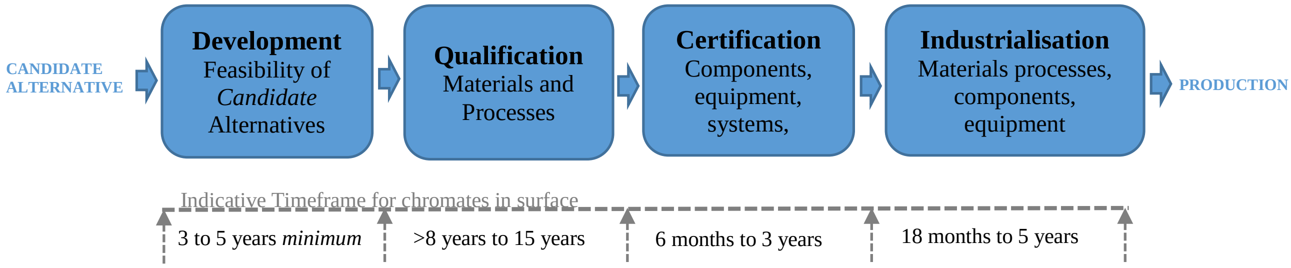
Ongoing development of potential alternatives for the aerospace sector

Assuming a technically feasible potential alternative is identified as a result of ongoing R&D, extensive effort is needed beyond that point before it can be considered an alternative to strontium chromate within the aerospace industry.

Aircraft are one of the safest and securest means of transportation, despite having to perform in extreme environments for extended timeframes. This is the result of high regulatory standards and safety requirements. The implications for substance substitution in the aerospace industry is described in detail in a report prepared by ECHA and EASA in 2014, which sets out a strong case for long review periods for the aerospace sector based on the airworthiness requirements deriving from EU Regulation No 216/2008. Performance specifications defined under this regulation drives the choice of substances to be used either directly in the aircraft or during the manufacturing and maintenance activities. It requires that all components, equipment, materials and processes incorporated in an aircraft must be qualified, certified and industrialised before production can commence. The process is illustrated in **Figure 3**. This system robustly ensures new technology and manufacturing processes can be considered ‘mission ready’ through a series of well-defined steps only completed with the actual application of the technology in its final form (and under mission conditions). When a substance used in a material, process, component, or equipment needs to be changed, this extensive system must be followed in order to comply with airworthiness requirements. The system for alternative development through qualification, certification, industrialization and implementation within the aerospace sector is mirrored in the defence and space sectors.

The detailed process involved in qualification, certification, and industrialisation, and the associated timeframes, are elaborated in Chapter 5. Of course, these steps can only proceed once a candidate alternative is identified. Referring to experience, it can take 20 to 25 years to identify and develop a new alternative, even assuming no drawbacks during the various stages of development of these alternatives. Experience over the last 30 years already shows this massively under-estimates the replacement time for chromate coating systems treatments. Taken together, available evidence clearly shows that no viable alternative for strontium chromate is expected for at least the next 10 or even 15 years.

Figure 3: Illustration of the development, qualification, certification and industrialisation process required in the aerospace sector.



As a further consideration, while the implications of the development process in the aeronautic and aerospace sectors are clearly extremely demanding, specification of an alternative, once available, can be built into the detailed specification for new aircraft types (and new spacecraft). This is not the situation for existing aircraft types, for which aircraft may still be in production and/or operation. Production, maintenance and repair of these models must use the processes and substances already specified following the extensive approval process. Substitution of strontium chromate-based surface treatment for these 'legacy' craft introduces yet another substantial challenge; re-certification of all relevant processes and materials. Unless Cr(VI)-free solution are considered as 1:1 replacements, it will be impractical and uneconomical to introduce such changes for many such aircraft types.

Table 2: Overview of key potential alternatives for corrosion-resistant coatings

Application	Matrix/Process	Cr(VI)-free corrosion inhibitors	Technical failure
Primer, specialty coatings	Epoxy / polyurethane-based primers†	Cr(VI)-free corrosion inhibitors (confidential)	• Corrosion resistance not sufficient • Adhesion not sufficient
		Organic corrosion inhibitors like 5-methyl-1H-benzotriazol	• Corrosion resistance not sufficient • Chemical resistance not sufficient
		Phosphate-based corrosion Inhibitors ‡	• Corrosion resistance not sufficient
		Magnesium-based corrosion inhibitors ‡	• Corrosion resistance not sufficient • Compatibility with various substrate not sufficient
	Electrocoat primer technology	Various ‡	• Corrosion resistance (long-term) not sufficient • MRO applications
	Silane-based coatings	Sol-gel coatings ‡	• Corrosion resistance not sufficient • Complex geometries

† with non-chromate inhibitors
‡ only some substances in this group may be considered possible alternatives

In this context, the scale and intensity of industry- and company- wide investment in R&D activity to identify alternatives to chromate surface treatment systems is very relevant to the findings of the AoA. Serious efforts to find replacements for chromates have been ongoing within the aerospace industry for over 30 years and there have been several major programs to investigate alternatives to chromates in the aerospace sector over the last 20 year

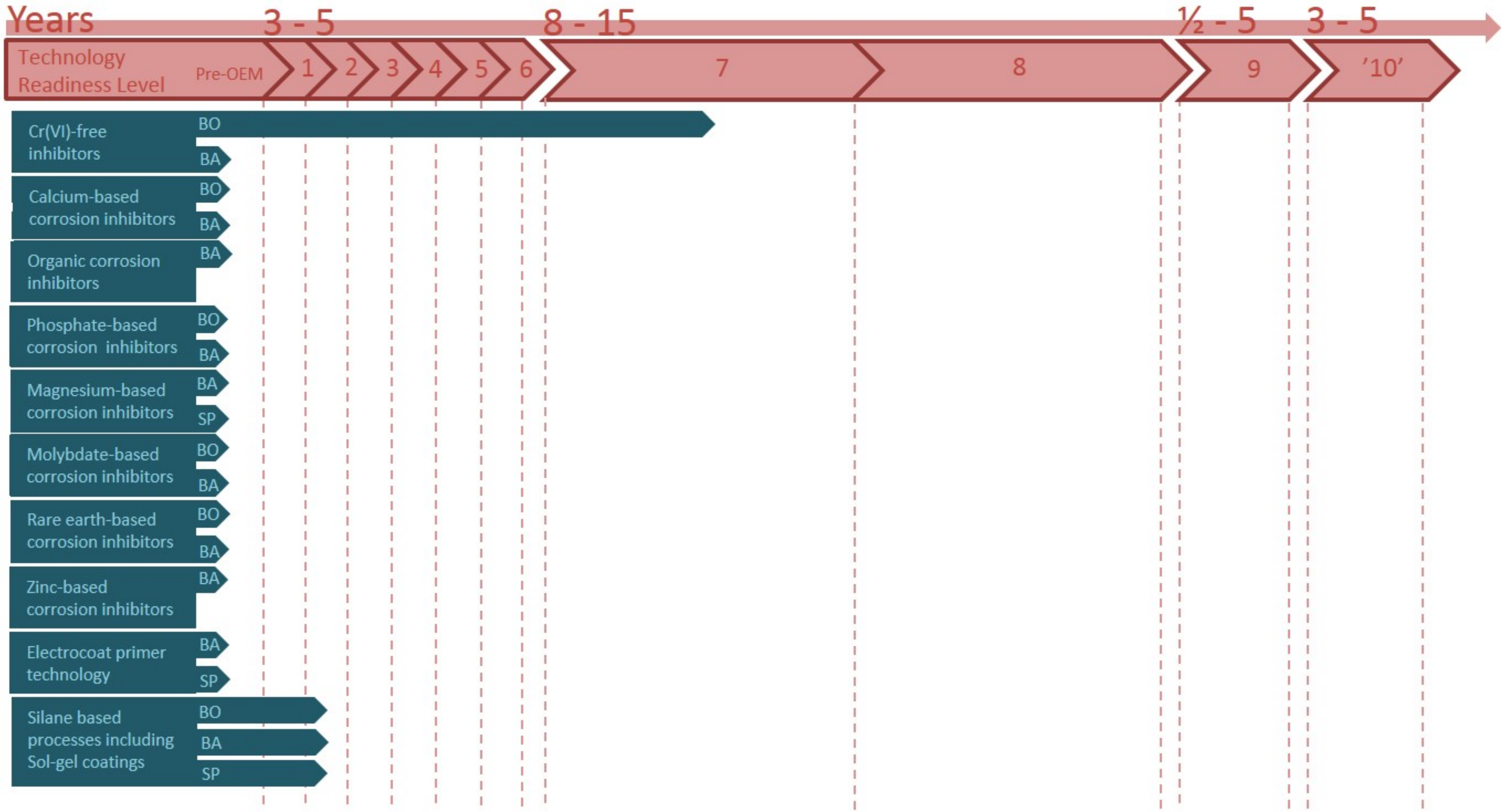


Figure 4: Development status of alternatives. BA: Basic primer; BO: Bonding primer; SP: structural primer.

Figure 4 gives an overview of the TR Level of potential surface treatment alternatives. It is important to note that those readiness levels are best case scenarios for single OEMs/applications only and do not reflect the general development status of the aerospace sector.

Concluding remarks

A large amount of research over the last 30 years has been deployed to identify and develop viable alternatives to Cr(VI)-based coatings. Due to its unique functionalities and performance, it is challenging and complex to replace surface treatments based on strontium chromate (or other chromates) in applications that demand superior performance for corrosion and/or adhesion to deliver safety over extended periods and extreme environmental conditions.

Several potential alternatives to strontium chromate-based coatings, such as various epoxy or polyurethane-based primers containing a range of different corrosion prevention agents, are under investigation for the aerospace industry, which expects to spend in excess of €200 million developing alternatives. However, based on experience and with reference to the status of R&D programs, alternatives are not foreseen to be commercially available for all key applications in this sector for at least 12 or 15 years.

2. INTRODUCTION

This AfA is the culmination of extraordinary effort across industry over several years to share data and prepare a comprehensive and reliable assessment of alternatives that is representative for the industry.

The aerospace industry recognises that the use of such sector-specific approach in an upstream application will facilitate assessment by the SEAC. Without this approach, multiple applications for authorisation utilising different approaches, assumptions and terminology are unavoidable; such differences could present challenges for enforcement across the industry.

The AoA is based on extensive input and data held by the aerospace sector, associated industries and third parties. The same companies and facilities have reviewed and validated the findings in detail and agree that the AoA is representative of the situation across the industry.

2.1. Substance

The following substance is the subject of this analysis of alternatives:

Table 3: Substances included in this analysis of alternatives.

#	Substance	Intrinsic property(ies)[1]	Latest application date[2]	Sunset date[3]
S6	Strontium chromate EC No: 232-142-6 CAS No: 7789-06-2	Carcinogenic (category 1B)	22.07.2017	22.01.2019

[1] Referred to in Article 57 of Regulation (EC) No. 1907/2006
[2] Date referred to in Article 58(1)(c)(ii) of Regulation (EC) No. 1907/2006
[3] Date referred to in Article 58(1)(c)(i) of Regulation (EC) No. 1907/2006

This substance is categorised as a substance of very high concern (SVHC) and is listed on Annex XIV of Regulation (EC) No 1907/2006. It is an inorganic chromate salt based on hexavalent chromium (Cr(VI)). Adverse effects are discussed in the CSR.

2.2. Uses of Cr(VI) containing substances

Cr(VI) containing substances have been widely used since the middle of the 20th century. The major uses in the aerospace sector are:

- Surface Treatment of metals such as aluminium, steel, zinc, magnesium, titanium, nickel, alloys;
- Sealing of anodic films and plating;
- Usage in metal primers, and various specialty coatings including but not limited to wash primers, and adhesive bonding primers;
- Formulation of mixtures for the above mentioned uses.

2.3. Purpose and benefits of Cr(VI) compounds

Using strontium chromate has multifunctional positive effects, especially due to the Cr(VI) compound. The following desirable properties of Cr(VI) have made this compound a State of the Art substance for a wide range of applications for more than 50 years:

- Excellent corrosion protection and prevention to nearly all corrosion sensitive metals in a wide range of environments. When a coating is damaged, such as a scratch that exposes the base material, the solubility properties of the chromates allow them to re-establishing a corrosion inhibiting layer by diffusion;
- Cr(VI) compounds have been demonstrated to provide biostatic properties, inhibiting the growth and proliferation of biological organisms.

The metallurgy, refractory, and chemical industries are fundamental users of Cr(VI). Furthermore, the aerospace, automobile, and military sectors depend on Cr(VI) to meet the very high requirements for products used under extreme conditions.

Several alternatives are being tested to replace strontium chromate. It is a challenge to find a substitute which meets all requirements for each use of a product, while also being technically and economically feasible.

3. ANALYSIS OF SUBSTANCE FUNCTION

Strontium chromate is used in the aerospace sector in paints, primers and specialty coatings which is illustrated in the following sections.

3.1. Usage

The main use of paints, primers, and specialty coatings in the aerospace sector is corrosion prevention. The complexity of aircraft or spacecraft construction makes corrosion prevention a very challenging task. Corrosion of metal surfaces can be influenced by a broad variety of factors, such as:

- Temperature;
- Humidity;
- Salinity of the environment;
- Industrial environment;
- Geometry of parts;
- Surface conditions;
- Erosion;
- Impurities;
- Stress;
- Chemical loads such as hydraulic fluids;
- Biological growth;
- Accumulated liquid;
- Operational fluids; or
- Galvanic coupling.

All the factors listed above can occur alone or in combinations under certain environments at different parts of an aircraft or spacecraft. Not all components of an aircraft are equally susceptible to corrosion, especially vulnerable components are known to include structural components such as the skin originating at lap joints as well as fasteners and fastener holes, landing gear, other structural components, and engine components. Other major areas susceptible to corrosion include where moisture and liquids are entrapped, such as under fairings. For spacecraft, external parts exposed to harsh environments (e.g. at launch pad at Guiana Space Centre, Kourou, French Guiana) interstage skirts and pyrotechnic equipment are susceptible to corrosion. However, corrosion prone areas also vary with the type of aircraft as shown in **Table 4**.

Table 4: Corrosion prone areas on different types of aircraft.

Civil Aircraft/Spacecraft	Fighter Aircraft	Helicopters
Main undercarriage	Missile and gun blast areas	Main rotor head assembly
Nose undercarriage	Engine intake areas	Tail rotor assembly
Rudder and elevator shroud areas	Cockpit frames	Transmission housing
Aileron and flap track area, flap tracks and trailing edges	Wing fold areas	Main rotor blades and leading edges
Access and freight doors	EMI/ Lightening Strike Shielding	EMI/ Lightening Strike Shielding

Civil Aircraft/Spacecraft	Fighter Aircraft	Helicopters
Control cables	LO Coatings	
Leading edges, hinge lines and air ducts	Structure for fighter on sea carrier	
Radome areas		
EMI/ Lightening Strike Shielding		
Pyrotechnic equipment		
Interstage skirts		

Importantly, in this demanding environment corrosion may still occur with the highly developed Cr(VI)-containing coating systems. For currently used coatings, decades of extensive experience exists relating to the appearance and impacts of corrosion. Without a well-developed Cr(VI)-free alternative, corrosion will certainly increase, as these alternative coatings do not offer all the crucial properties of Cr(VI) coating systems and their long-term performance can currently only be estimated. Likely, the corrosion problems would not appear suddenly but only after several years, when hundreds of aircraft are delivered. Re-equipping, if possible, would cost hundreds of million €. As a consequence, decreased corrosion protection performance may lead to shorter inspection intervals, which has a significant impact on the maintenance costs for aircraft. Furthermore, for secure adaptation of the inspection intervals a detailed knowledge of the alternatives is a prerequisite. Some of the corrosion prone areas, as well as further examples on parts requiring corrosion protection are illustrated in **Figures 5-12** below:

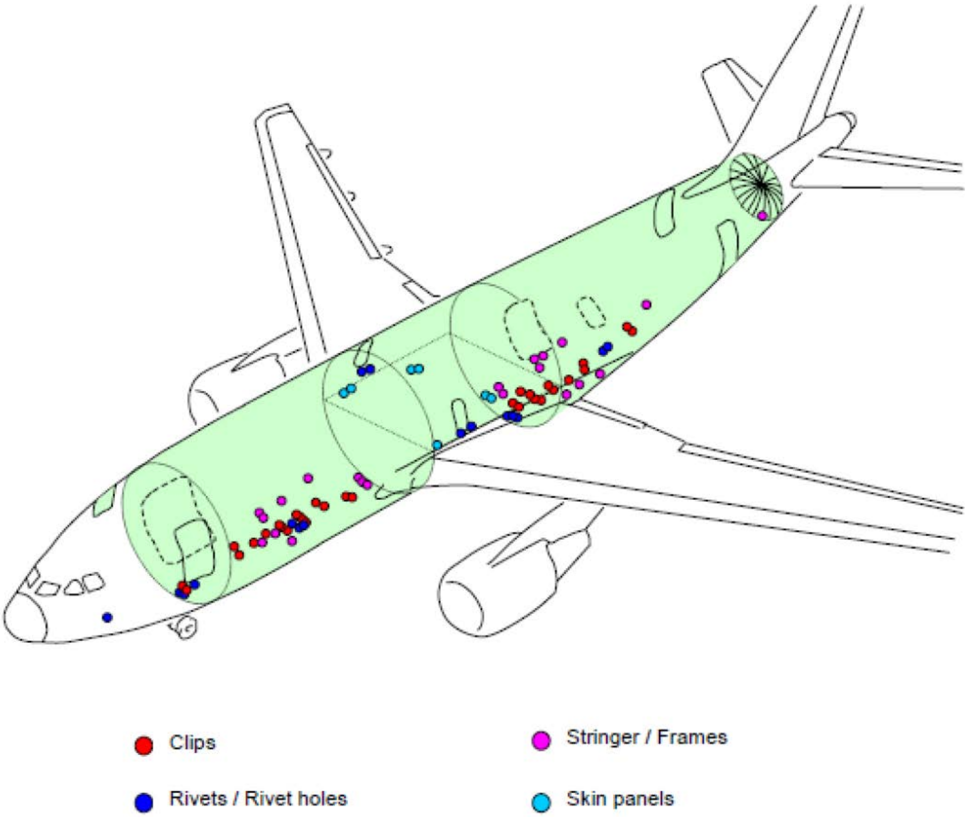


Figure 5. Schematic illustration of typical corrosion findings in an aircraft fuselage (Airbus)

Figure 6: ATR 600 aircraft & Gulfstream V aircraft (UTC Aerospace Systems – Propeller Systems, 2014)

Figure 7: Propellers mounted on an aircraft. (UTC Aerospace Systems – Propeller Systems, 2014)

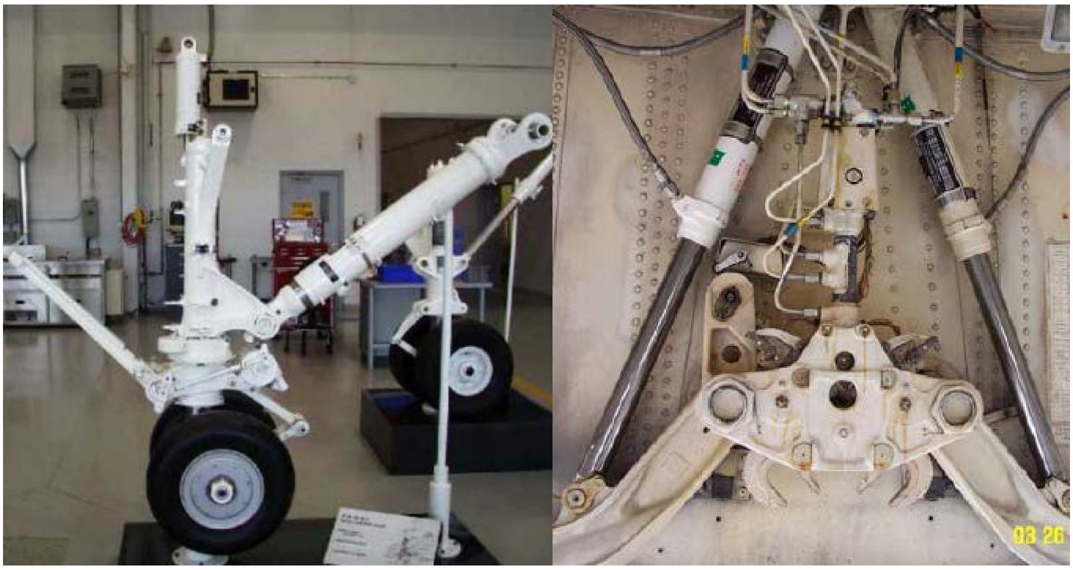


Figure 8: Undercarriage - landing gear, examples (Rowan Technology Group, 2005)

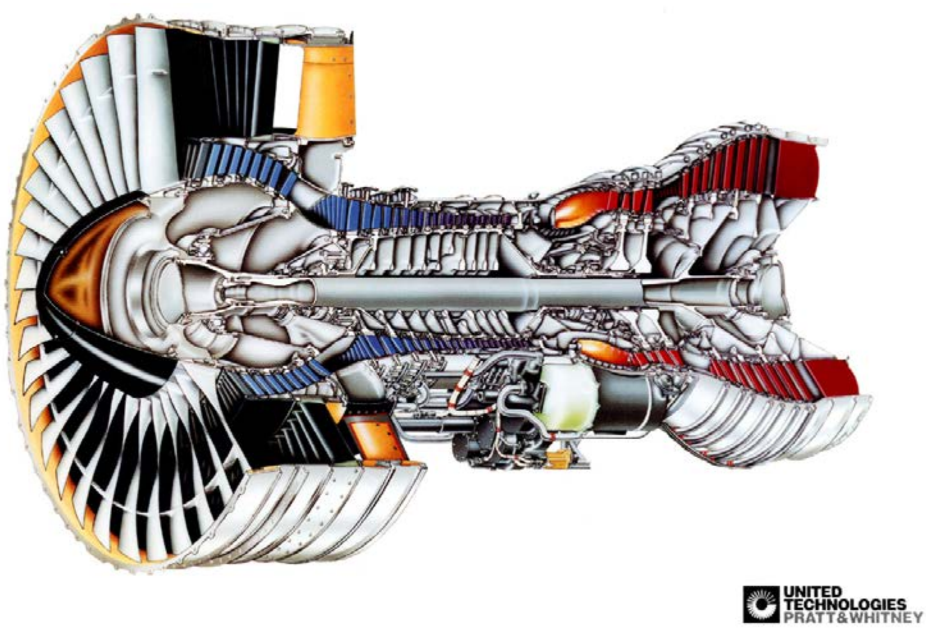


Figure 9: Gas Turbine Engine sketch example of PW4000 92 inch fan engine (UTC – Pratt & Whitney Divison)

Figure 10: Emergency door damper for a civil aircraft. (UTC Aerospace Systems – Propeller Systems, 2014)

Figure 11: Main & tail rotor shaft elements of a helicopter (UTC Aerospace Systems – Propeller Systems, 2014).

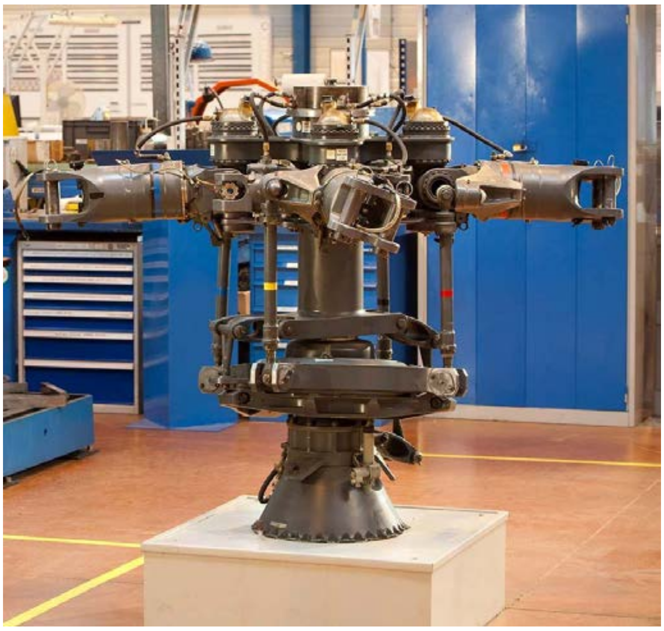


Figure 12: Partially assembled main helicopter rotor. (UTC Aerospace Systems – Propeller Systems, 2014).

Different kinds of corrosion occur at these prone areas with some of the most common being illustrated in the following paragraphs.

Fastener and fastener holes are well known to be susceptible areas for different kinds of corrosion. Galvanic, filiform and crevice corrosion can occur at fasteners in contact with the aircraft skin (dissimilar metal). Stress corrosion cracking is also applicable as fasteners have to withstand stresses or loads.

Corrosion fatigue and stress corrosion cracking may develop around fastener holes due to stress concentration at a single point in the hole, and also on structural components which have to withstand stress and are exposed to corrosive environments.

Grain boundary corrosion or intercrystalline corrosion is the main type of corrosion in high strength aluminium alloy parts and for corrosion fatigue.

Exfoliation corrosion may occur in materials that are susceptible to this form of corrosion (such as crevices of thick extruded or rolled aluminium plate). The potential for exfoliation corrosion to occur is increased at unprotected panel edges where end-grain is exposed. This is also true for other exposed metal areas such as countersinks.

Fretting corrosion occurs when overlapping metallic joints are subject to repeated or cyclic relative movement and where a corrosive environment is present

Treating surfaces susceptible to corrosion with Cr(VI) containing products provides, in combination with the correct choice of material, the required corrosion prevention properties and functionality.

Any structural detail where there is an unsealed gap between adjacent components where moisture can become entrapped (like a joint) is highly susceptible to corrosion. Protection can be provided by priming these surfaces adequately. Again the use of hexavalent chromates has proved to be most effective for this purpose.

Electrical systems are often subject to corrosion at wires, connectors and contacts, especially where moisture or humid environments are present.

Highly corrosive environments are also present in aircraft engines during operations caused by high temperatures and the presence of corrosive gases and liquids. Accelerated forms of corrosion can be found at the engine air inlet where airborne solids or rain erosion can damage the metal and coating surfaces. Similar highly corrosive environments are present in helicopter components such as rotor heads, and main and tail rotor blades.

There are many more areas which are prone to corrosion in an aircraft. The following list provides a rough overview but is far from being complete:

- Bilge areas where wastes of all kinds are collected(– e.g. hydraulic fluids, water, dirt);
- Control surface actuating rods and fittings may corrode as a consequence of coupling with dissimilar metals, being damaged, or deteriorated protective coatings;
- Undercarriage bays (i.e. area of the wheel wells) are affected by debris from the runway;
- Battery compartments and vent openings due to battery spillage;
- Fuel tanks due to the ingress of moisture and resulting microorganisms that can reside in fuel;
- Engine exhaust trail areas affected by exhaust gases;
- Galley and lavatory areas are affected by spilled foods and human waste;and
- Cargo areas collect all kinds of miscellaneous corrosive materials brought in by the cargo containers (e.g. mud, salt, oils, water, livestock waste, chemical spills, food products, etc.).

In this introduction, only examples of corrosion were presented. However, there is often a combination of certain properties required for these parts.

3.2. Categories

The main uses of strontium chromate in primers and specialty coatings are for metallic materials and alloys, especially for steel, aluminium, magnesium, nickel, and cobalt. The aerospace sector uses Cr(VI) primarily with lightweight metals and alloys such as aluminium and magnesium. Within the context of this dossier a primer is a corrosion-inhibiting coating which is applied as the first complete coat. It must provide maximum adhesion both to the substrate and to any subsequent coating layers / top coat. The use of these coating systems is an effective and well-established way to prevent or retard corrosion in the aerospace sector.

All coatings categorised below are low viscosity dispersions of solid components in a blend of various liquids which are composed of three main components:

The first component of the kit is the binder or base. It serves as the matrix, and is usually composed of a synthetic resin. Typical resins are epoxies, alkyds and polyurethanes due to their excellent adhesion properties and resistance to exposure to a range of aerospace fluids. The strontium chromate is dispersed and held in suspension in the liquid binder.

The second component of the kit is the catalyst. In multicomponent products, the resin will be cured/crosslinked by combining it with a curing agent such as a polyisocyanate or polyamine. The rate of the reaction is usually controlled by the catalyst.

The third component is the solvent or thinner. This can be either an organic solvent, water, or a combination of both. The thinner controls the viscosity of the liquid/solid dispersion. Solvents represent a volatile component and evaporate into the atmosphere after the primer is applied.

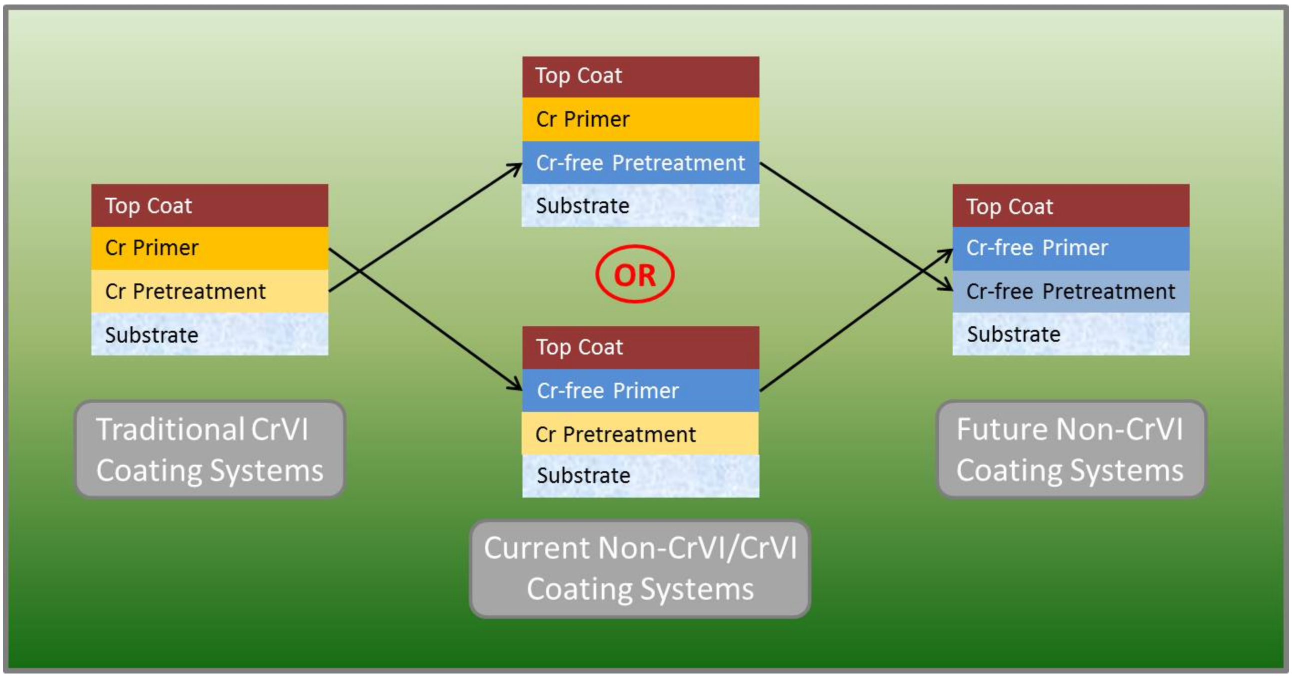


Figure 13: Development of coating systems – from the past to the future (**AMMTIAC 2012, amended**

Besides the three main compounds mentioned above other additives may be used as part of the formulation to control, for example, the rheology of the dispersion, the rate of reaction in a multicomponent system, the adhesion to a range of substrates or the flow and surface wetting of the applied product.

All non-volatile components react or coalescence together and form a uniform film.

In the aerospace sector the primers and specialty coatings can be differentiated as described in the following chapters. This listing is indicative and not exhaustive.

3.2.1. Primer and basic primer

Primer means the first layer and any subsequent layers of identically formulated coating applied to the surface of an aerospace vehicle or component. Primers are typically used for corrosion prevention, protection from the environment, functional fluid resistance, and adhesion of subsequent coatings. Primers that are defined as specialty coatings are not included under this definition.

Primers are a pigmented composition of liquid consistency applied as a thin layer which converts to a solid, adherent and tough film.

Basic primers represent the largest volume primer coating due to their universal applicability to many substrates and compatibility with many subsequent coatings. Cr(VI)-based basic primers have been used for decades to coat metallic parts. Basic primers or paint primers are also sometimes called “green primers” because the typical colour is green. Their main purpose is corrosion protection although they must simultaneously provide good adhesion between the metal surface and further coating layers. Basic primers must be compatible with any subsequent layer applied to it.

An absolutely clean surface is necessary for a long-term paint adhesion to obtain the desired corrosion protection.

Basic primers are applied as basic layer of a multi-layer paint or coating system which is illustrated in **Figure 14**:

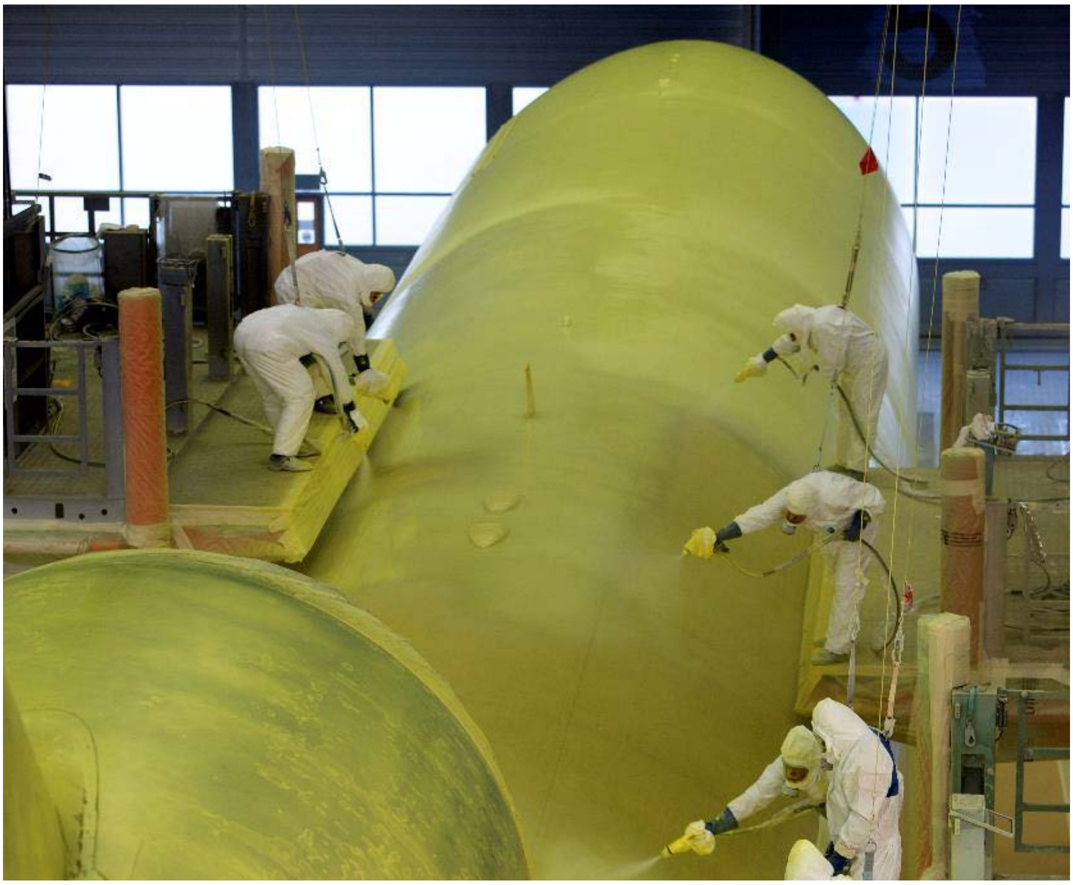


Figure 14: Application of a primer.

In addition to their corrosion inhibition functionality they are characterised by excellent adhesion properties and chemical resistance.

3.2.2. Specialty coatings

A specialty (or speciality) coating is a coating that, even though it meets the definition of a primer, topcoat, or self-priming topcoat, has additional performance criteria beyond those of primers, topcoats, and self-priming topcoats for specific applications. These performance criteria may include, but are not limited to, temperature or fire resistance, substrate compatibility, antireflection, temporary protection or marking, sealing, adhesively joining substrates, or enhanced corrosion protection.

Specialty coatings in this dossier are not limited to the ones listed in Aerospace Control Techniques Guideline (CTG), Appendix A (EPA, 1997). They also include specialized function coatings which fulfil extremely specific engineering requirements that are limited in application and are characterized by low volume usage. These materials have wide variation in performance requirements and are not interchangeable.

Strontium chromate is used in a broad range of specialty coatings. The most common are illustrated in more detail below.

3.2.2.1 Adhesive bonding primer

Adhesive bonding involves joining together two or more metal or nonmetal components. This process is typically performed when the joints being formed are essential to the structural integrity of the aerospace vehicle or component. Bonding surfaces are typically roughened mechanically or etched chemically to provide increased surface area for bonding and then treated chemically to provide a stable corrosion-resistant oxide layer. The surfaces are then thinly coated with an adhesive bonding primer to promote adhesion and protect from subsequent corrosion. Structural adhesives are applied as either a thin film or as a paste. The parts are joined together and cured either at ambient temperature, in an oven, or in an autoclave to provide a permanent bond between the components (EPA, 1997).

Typical bonding structures in the aerospace sector are upper parts of an airplane / helicopter, e.g. glare foils with a thin aluminium sheet bonded with a glass fibre on top. Rear parts of airplanes are hexagonal aluminium bonded.

Figure 15: Bonding primer applied on the propeller tulip in green (left) which contributes to the bonding performance between the tulip and the composite blade (right). (UTC Aerospace Systems – Propeller Systems, 2014).

3.2.2.2 Structural primer

Commercial exterior aerodynamic structure primers is a specialty coating used on aerodynamic components and structures that protrude from the fuselage for the purpose of extended corrosion protection and enhanced adhesion. This primer has higher adhesion requirements designed to withstand erosion from impingement of rain at the leading edges of the aircraft. For example; wings and attached components, control surfaces, horizontal stabilizers, vertical fins, wing-to-body fairings, antennae, and landing gear and doors.

3.2.2.3 Fuel tank primer

Fuel tank coatings are applied to fuel tank components for the purpose of corrosion and/or bacterial growth inhibition and to assure sealant adhesion in extreme environmental conditions.

Fuel tank primers have a very specific and important role as a primer system in fuel cells and fuel tank components, which are exposed to a very harsh environment due to the presence of water and microbes.

3.3. Process description

All above mentioned products are used during the manufacturing cycle of aircraft and spacecraft as well as in maintenance. Products are applied in both dedicated booths and in workshops. All primers mentioned in chapter 3.2, and paints are applied by hand held or automated spraying guns, rollers, brushes or by dipping, immersion, or pen sticks.

Dipping or immersion application takes place in large facilities or large repair stations where the part is dipped into a tank filled with the coating material.

Brushing, rolling or pen sticks are used for smaller repair work and on surfaces which are not suitable for a spraying process.

Spraying is a very common and cost effective technique to cover large surfaces with a uniform coating layer. Spray guns with an integral paint container are used for small areas whereas pressure-feed guns are most efficient for large areas, as a large amount of coating material needs to be continuously applied without interruption. Spray guns used in the industry are designed to maximize transfer efficiency which also reduces exposure to workers. All sizes of parts can be processed: from very small parts, e.g. a ball screw, up to whole airplanes.

The sensitivity to temperature and relative humidity of primer depends on their chemical formulation. Some primers are applied and cured under room temperature and other parts/aircraft may be heated to accelerate curing of the coating.

The selection of coating products, the number of coatings in a given system and the number of paint layers is determined by the design of the component or structure, the materials used in the manufacture of the component, the nature of the structure which the component interfaces and the environment in which the component/structure will operate.

The coating process is illustrated in the following figures **Figure 16 –Figure 17**:

Figure 16: Application of a coating layer with a hand-held spray gun, example 1.

Figure 17: Application of a coating layer with a high volume low pressure (HVLP) hand-held spray gun, example 2.

3.4. Strontium chromate – substance specific characteristics

Corrosion resistance is one of the major functionalities of chromates in surface treatment processes. Strontium chromate is used as an anticorrosive primer component in surface treatment processes for a variety of substrates including aluminium, ferrous and magnesium alloys and steels to offer long term environmental protection for those substrates especially in the following applications:

- where extreme exterior weathering and aggressive environmental conditions require high-end corrosion protection; and
- within the aircraft internal structure, due to media, temperature and humidity changes.

3.4.1. Key physical-chemical quality parameters for corrosion inhibitors

Corrosion inhibitors can be categorised according to basic quality criteria including inhibitive efficiency and versatility, toxicity, and price. Ideally, the corrosion inhibitor is compatible with all primer, paint, and specialty coating systems and performs effectively on all typical metal substrates. Furthermore it has to guarantee product stability (chemically, thermally, and regarding particle size distribution), reinforce the useful coating properties and needs to have reasonable rheological behaviour in the paint / primer formulation. Thus, high assay and low content of soluble contaminants such as chloride and sulfide anions are required as well.

Strontium chromate is used as a corrosion inhibitor incorporated into the paint, primer and specialty coating system. Strontium chromate is extremely effective at low loadings. Corrosion inhibitive particles of strontium chromate are only effective in solution. The level of solubility is related to the protection against corrosion.

In order to provide the desired functionality, strontium chromate must be available in sufficient quantities, at a sufficient concentration and with appropriate mobility properties to reach an unprotected/scratched area on the material to modify or prevent the corrosion process.

3.4.2. Physical-chemical characteristics and properties of strontium chromate

Strontium Chromate is one of the most effective and valuable inorganic corrosion inhibitors in paints, primers, and specialty coatings since early 1960's.

Physical and chemical characteristics of strontium chromate are summarised in **Table 5**:

Table 5: Strontium Chromate chemical and physical properties.

Parameter	**Value**
Water solubility $SrCrO_4$	1.2 g/L (15° C)
Appearance	Yellow, odourless powder
Specific gravity	3.8 g/cm³
pH value	7.5
Oil absorption	24 cm³/100g
Sr as SrO content	48 %
Cr as CrO_3	46 %
Moisture content – 1h at 105°C	Typ. 1.0 %
Conductivity	<1100 µS/cm
Sieve residue on a 45 µm	<1.0 %
Granulometry	3.64 µm
Decomposition	500°C

3.5. Key chromate functionalities

The basic functions of a surface protection system are the combination of the physical barrier function provided by the passive layers and the active features of chemical corrosion inhibition of the free surface after damage which is illustrated in **Figure 18** and described below:

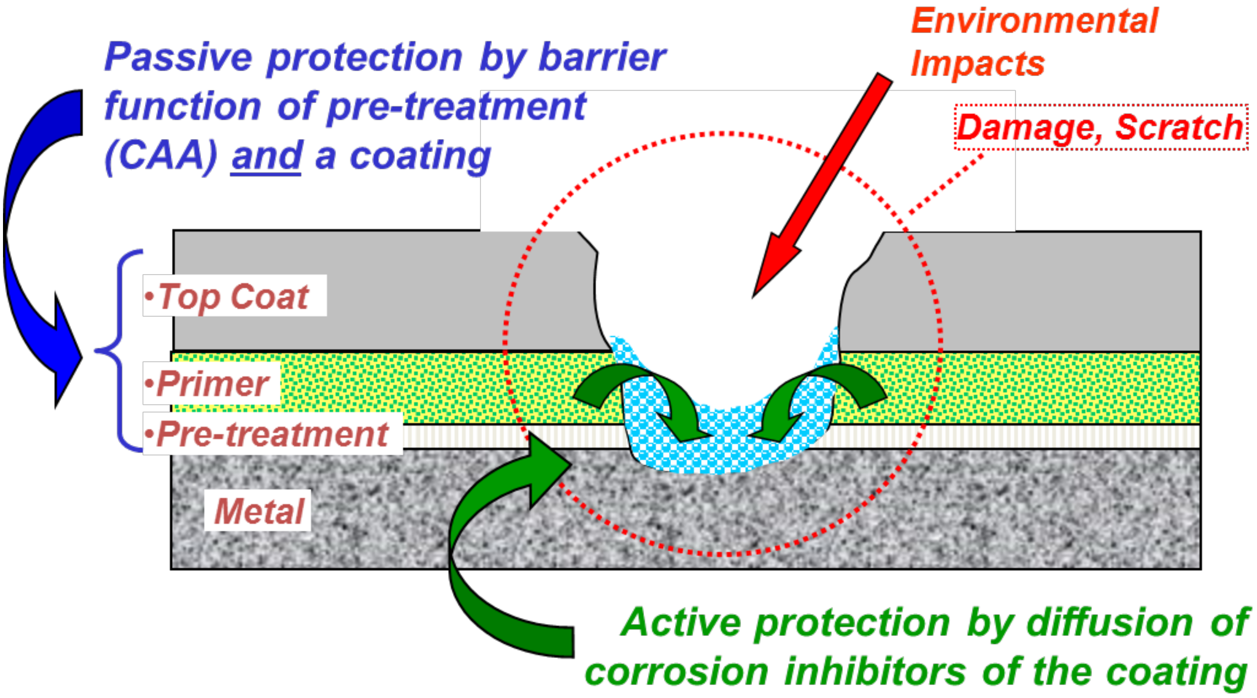


Figure 18: Basic functions of a surface protection system (Airbus S.A.S. 2014).

Cr(VI) has two-fold corrosion inhibition properties. Firstly it combines with the naturally occurring aluminium oxide to form a chromium oxide layer that, by sitting on top of the aluminium, prevents oxygen from contacting the aluminium and thus provides a corrosion inhibition layer (the principle is not dissimilar to that of Stainless Steel where surface oxides, of Ni and Cr, prevent oxygen attacking the base metal, Fe). Secondly, should the chromium oxide layer be damaged (e.g. scratched sufficiently deeply to reveal bare aluminium) then, after the initial creation of a thin aluminium oxide layer, the Cr(VI) ion, in its hydrated form, diffuses into the aluminium oxide converting it to chromium oxide thus re-establishing a corrosion inhibiting layer albeit a layer that is less effective than before. The areas close to the “scratch” will become depleted in Cr(VI) thus reducing the corrosion protection offered in the immediate area. However, the diffusion mechanism operates continuously allowing further diffusion of Cr(VI) ions from more distant areas into the depleted area. This dynamic process represents the “self healing” mechanism that to date, appears to be unique to Cr(VI).

Chromates are unique with respect to the efficiency/concentration ratio not achieved with other compounds. These unique functionalities of Cr(VI) make it an ideal and not easily replaceable substance in primers, paints, and specialty coatings, which can be illustrated in **Figure 19** with an aluminium alloy substrate, a typical material used in the aerospace sector. Moreover their solubility and diffusion-rate can be adjusted by selection of the cation.

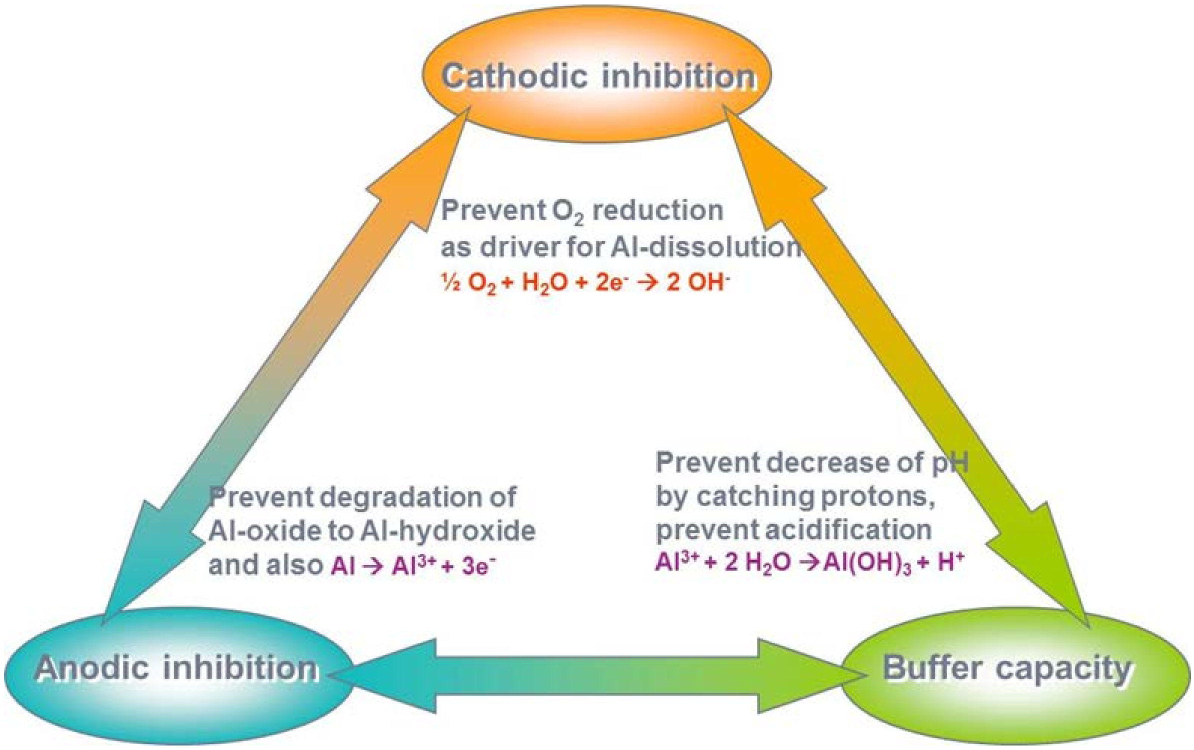


Figure 19: Key chromate functionalities illustrated with exemplary aluminium substrate (Airbus S.A.S, 2014).

- Chromate corrosion inhibitors release chromate ions in a characteristic way when they are suspended in a medium and applied as a coating. Cr(VI) provides **cathodic corrosion inhibition** by preventing the reduction of O_2 as the driver for Al-dissolution: ($1/2\ O_2 + H_2O + 2e^- \rightarrow 2\ OH^-$) and by blocking the copper from the high strength alloys in the noble phases.
- Cr(VI) provides **anodic corrosion inhibition** by preventing the degradation of Al-oxide to Al-hydroxide and also $Al \rightarrow Al^{3+} + 3e^-$ which is the actual corrosion process.
- Cr(VI) provides an excellent **buffer capacity**, preventing the acidification of the aluminium surface by catching protons, $Al + 2\ H_2O \rightarrow Al(OH)_3 + H^+$, thus increasing the electrical resistance of the metallic surface.

Strontium chromate has been determined to be extremely effective in protecting gaps and cut edges against corrosion. Several tests have proved that the solubility of strontium chromate is sufficient to provide an adequate supply of inhibitive ions.

The predicted level of protection as a function of concentration is calculated from a diffusion-rate curve obtained under arbitrary immersed conditions. In general, a low concentration of strontium chromate ions (between 1 and 10 ppm) is deemed sufficient for most uses and processes. However, certain applications may have higher needs of concentrations in the range of 1000 ppm, especially in the initial phase followed by a significant decrease to a fairly steady level state with continuous supply of low concentrations. This is in line with ideal curves of effective primers identified for typical use on aircraft. The correct diffusion-rate is very important as high solubility can lead to blistering and low solubility may not supply sufficient chromate ions.

The level of required corrosion protection can vary for different application areas. For example bore holes or discontinuities require an initial high concentration of strontium chromate together with a steady diffusion mechanism which is high enough to ensure protection without excessive loss of chromate, which could cause premature degradation of the primer layer.

The protection requirements for many parts of an aircraft or spacecraft are very high and can be combined into one general category. The characteristics of strontium chromate have passed the specification thresholds for this category to be applied in primers on aircraft and have been proved to be effective against corrosion.

3.6. Key technical criteria

It should be noted that while the numerical values reported for key requirements here have been supplied by industry, they are not necessarily the same for all companies. Furthermore, requirements for individual applications may also vary. The key technical criteria which affect the suitability of alternatives to using strontium chromate in paints, primers, and specialty coatings are as follows:

Table 6: Key technical criteria which affect the suitability of alternatives to using Cr(VI) in paints, primers, and specialty coatings.

Application	**Quantifiable key functionality**	**Requirements**
Primer, specialty coatings	Corrosion resistance	*Basic primer:* • 500-3000 h on various substrates (e.g. Mg alloys, steel, Al/Ti) (ISO 9227) • 3000 h on Al alloys (ISO 9227) • 960-3000 h, length from scratch 0.5-2 mm (Filiform corrosion test, EN 3665) • long-term requirements up to 9000 h on Al alloys, <1.5 mm scratch (ASTM B117, ISO 7253) *-Bonding primer:* • 3000 – 6000 h (ISO 7253)
	Adhesion of paint / compatibility with binder system	GT 0-1 under dry conditions (Cross-cut Test, ISO 2409 / ASTM 3359), most aerospace companies require GT0
	Layer thickness	*Basic primer* 10-30 µm (5 µm for special applications) *Bonding primer* 2-12 µm
	Chemical resistance	No blistering or delamination after 1000 h at 70 °C to hydraulic fluids (ISO 2812, 1200 g)
	Temperature resistance (thermal shock resistance)	No cracks or peeling (GT<1) after 24 h at -55 °C and 150 °C (BS 2X 33, PR EN 4160, HMDC 0097A)
	Compatibility with substrate	Compatibility with all metallic substrates and surface treatments as well as composites (ISO 2409)
	Processing temperatures	Ability to be processed/ implemented at room temperature

Corrosion resistance

Corrosion describes the process of oxidation of a metallic material due to chemical reactions with its surroundings, such as humidity but also corrosive electrolytes. In this context, the parameter corrosion resistance means the ability of a metal aircraft part to withstand gradual destruction by chemical reaction with its environment. For the aerospace sector, this parameter is one of the most important since meeting its minimum requirements plays a key role in assuring the longest possible life cycle of aircraft/spacecraft and all the implicit parts, the feasibility of repairing and maintenance activities and most importantly, the safety of all air travellers or space components. Especially the AA2024 aluminium alloy, most commonly used in the aerospace sector, contains app. 5% of Cu as alloying element to provide the material strength. But Cu as noble element, acts as bulid in corrosion driver. Inhibition of the Cu is mandatory for long-term corrosion stability. The corrosion requirements vary within the aerospace sector and are depending on the metal substrate (aluminium alloy, steel type) and the coating thickness. Some key examples are provided below.

Corrosion inhibiting components can be categorized according to basic quality criteria including inhibitive efficiency and versatility and toxicity. Ideally, the component is applicable in all surface treatment processes, compatible with subsequent layers and performs effectively on all typical metal substrates. Furthermore it has to guarantee product stability (chemically and thermally) and has to reinforce the useful coating properties.

The ability of a material to spontaneously repair small amounts of chemical or mechanical damage is known as an active corrosion inhibition or self-healing property. If this characteristic is provided by a certain material, it is tremendously advantageous and will enhance service life duration of parts, maintenance intervals and on-flight security of air travellers.

Cr(VI) shows active corrosion inhibiting properties: if a surface is scratched, the Cr(VI) ion, in its hydrated form, diffuses into the surface oxide converting it to chromium oxide thus re-establishing a corrosion inhibiting layer (“active corrosion inhibition”). Moreover, this diffusion process also takes place even if the corrosion already started, leading to the corrosion process being significantly reduced or prevented. The active corrosion inhibiting properties are generally tested in line with the corrosion resistance based on the same test methods and requirements, as the active corrosion inhibition of a coating is a characteristic feature.

Industry requirements: The most commonly used test methods to determine corrosion performance of primer, paints, and paints are ASTM B117 and ISO 9227 (both Neutral Salt Spray Tests), ISO 7253 (Salt Spray Test) and EN 3665 (filiform corrosion test).

For **basic primer** applications, standard requirements range from 500 – 3000 h depending on the substrate. While for steel and magnesium 500-1500 h are sufficient, Al alloys require 3000 h. When testing according to EN3665, aerospace companies reported that length from scratch shall not exceed 0.5-2 mm after 960-3000 h. Additional long-term exposure testing up to 9000 h are required with maximum 1.5 mm corrosion from scratch.

For **bonding primer**, the requirements in ISO 7253 (Salt Spray Test) are in the range from 3000 to 6000 h (long-term corrosion).

Besides the standard corrosion tests, further extended corrosion tests with far higher demands and tests with higher in-service relevance are necessary. These extended tests take into consideration aspects of the real environment where the end products/pieces find their application.

Adhesion

Depending on the final functions of the components, they may be coated with protective layers to enhance visual appeal and protection against environmental conditions. In this analysis, the parameter adhesion describes the tendency of dissimilar particles or surfaces to cling to one another. In the aerospace industry, many parts are exposed to harsh environmental conditions, often in contact with other metallic parts, and are subjected to strong mechanical forces. It is of extreme importance that the coatings applied to these parts can withstand these effects and keep functioning properly for the longest period possible. For example rain erosion resistance is part of the adhesion tests, which emulates forces of high speed exposure at the leading edges of surfaces. It is of note, that the adhesion properties of a primer formulation are influenced by different factors and the complex interplay between corrosion inhibitor, matrix and other additives.

Industry requirements: In general, minimum requirements for the performance parameter adhesion (ISO 2409 and ASTM 3359) lie between GT0 and GT1. Under dry conditions many aerospace applications strictly require GT0, meaning essentially no loss of adhesion. After immersion to different media, GT<1 (less than 5% chipped of surface) is required.

Layer thickness

The thickness of the different layers or coatings on the substrate (defined in nanometres or micrometres) is also crucial for the best performance of all parts of the aircraft. The objective is to get maximum performance with minimum thickness which equates to weight. Weight is critical for fuel efficiency of aircraft. Not meeting the specified requirements of this parameter could lead to deficiencies in other characteristics of the pieces, for example reduced corrosion and chemical resistance, improper adhesion of coatings to the substrate or decreased cracking resistance. The process capability of Cr(VI)-free paint systems therefore needs to be considered in order to guarantee even coverage of 3 dimensional geometries.

Industry requirements: The most relevant method for the assessment of layer thickness is the ISO 2808. For bonding primer, a thickness between 2-12 µm is favourable, while for basic primer thicker layers between 10-30 µm are recommended.

Chemical resistance

This parameter is defined as the ability of solid materials to resist damage by chemical reactivity or exposure. For aerospace applications, it is highly important that all parts withstand contact with different chemicals such as de-icing fluids, greases, oils and lubricants and particularly aggressive fire resistant aviation hydraulic fluids. The chemical modification of protective coatings or the metal parts themselves could significantly increase maintenance costs and may sacrifice to some extent travel security.

Industry requirements: Most commonly used test method reported during the consultation is ISO 2812 (resistance to fluids). The resistance to hydraulic fluid (Skydrol LD-4) has to be > 1000 h at 70 °C. No blistering or delamination has to be detected and hardness has to be min. 1200 gram.

Temperature resistance (thermal shock resistance)

This parameter describes the ability of a material, in this context mostly referring to coatings, primers and paints, to withstand repeated low and high temperature cycling. For the same reasons stated above, it is indispensable that parts and coatings are able to perform their functions optimally at all temperatures to which the parts are going to be exposed during their service life.

Industry requirements: In general, different methods are available within the aerospace sector, where airframe components have to meet test requirements to operate at up to 150 °C and down to -55 °C for 24 h (BS 2X 33, PR EN 4160, HMDC 0097A). For some applications, requirements are even more stringent with temperatures up to 200°C and extended exposure.

Compatibility with substrates/other coatings

Compatibility with a wide range of substrates and primers is a key performance characteristic within the aerospace sector.

Industry requirements: To determine the compatibility with substrates or topcoats, adhesion testing according to ISO 2409 is carried out. In general, minimum requirements lie between GT0 and GT1. Under dry conditions many aerospace applications strictly require GT0, meaning essentially no loss of adhesion. After immersion to different media, GT<1 (less than 5% chipped of surface) is required.

4. ANNUAL TONNAGE

4.1. Annual tonnage band of strontium chromate

The confidential average tonnage for the use of strontium chromate in paints, primers, and specialty coatings is 200 tonnes per year.

The annual tonnage band for the use of strontium chromate in paints, primers and specialty coatings is *1-10 tonnes per year / 10-100 tonnes per year/ 100-1000 tonnes per year/ >1000 tonnes per year* tonnes per year.

5. GENERAL OVERVIEW ON THE SPECIFIC APPROVAL PROCESS IN THE AEROSPACE SECTOR

Much has already been written about the airworthiness and approvals process in the aerospace industry in the document “An elaboration of key aspects of the authorisation process in the context of aviation industry“ published in April 2014 by ECHA and EASA. The document makes a strong case for justification of long review periods for the aerospace sector. In this section we identify key points from the ECHA EASA “elaboration” document and add additional detail and justification for long review periods with specific regard to chromates.

Some of the key points identified in the “elaboration” document are:

- “The aerospace industry must comply with the airworthiness requirements derived from EU Regulation No 216/2008 in Europe, and with similar airworthiness requirements in all countries where aeronautical products are sold.”
- “All components, from seats and galleys to bolts, equipment, materials and processes incorporated in an aircraft fulfil specific functions and must be qualified, certified and industrialised.” In addition the new materials must be developed and evaluated prior to these three steps.
- “If a substance used in a material, process, component, or equipment, needs to be changed, this extensive process [of development, qualification, certification and industrialization] has to be followed in order to be compliant with the airworthiness requirements.”
- “Although the airworthiness regulations (and associated Certification Specifications) do not specify materials or substances to be used, they set performance specifications to be met (e.g. fire testing protocols, loads to be sustained, damage tolerance, corrosion control, etc.). These performance specifications will drive the choice of substances to be used either directly in the aircraft or during the manufacturing and maintenance activities.” In addition, a further point of clarification, it is not the substance that is chosen but rather the material and process.
- The development (TRL (Technology Readiness Level) 1-6) process “is an extensive internal approval process with many different steps from basic technology research up to technology demonstration in a lab environment.”
- “Depending upon the difficulty of the technical requirements [qualification] can easily take 3-5 years. After initial laboratory testing, each specific application must be reviewed, which means additional testing for specific applications / parts. Airworthiness Certification begins at this same time, this certification can take from 6 months to years. Additional time is needed for production scale-up and development of a supply chain.”

Each one of these points is of significant importance for the aerospace sector with regards to chromates. Further elaboration will be made within this section.

The last bullet point highlights that it can take a significant period of time to develop and implement new alternatives. It should be noted that in the case of chromates, the stated time needed for taking an alternative from the development phase through qualification, certification and implementation has been significantly underestimated. Efforts to find replacements for chromates have been ongoing within the aerospace industry for over 30 years. In this time some successful substitutions have been made, but large challenges remain. Efforts thus far to identify equivalents for substances with critical, unique properties like corrosion inhibition have proven that there are no ‘drop-in’ replacement substances for hexavalent chromium. Depending on the specific application and performance requirements many more years may be required before alternatives are identified and implemented.

In this section the general process for alternative development through qualification, certification, industrialization and implementation within the aviation sector is described. This process is also followed closely by the military and space sectors. The long-term operations of aviation applications is similar to the space industry. In the case of space industry the lifecycle depends on the type of spacecraft (military or civil launchers, satellites etc.) but it can be at least as complex and challenging as aircraft regarding: lifecycle duration, environment exposure and high requirements. The space sector is a highly valuable sector and a major political concern as the EU wants to have its own capacity to access to space (for example major programs such as Ariane 5, Vega, and all satellite programs for earth observation and telecommunications). Apart from the complexity of the supply, the aerospace sector faces particular unique challenges related to the operating environment, compliance with the airworthiness requirements and spacecraft requirements and the longevity of an aircraft and spacecraft that constrain its ability to adopt changes in materials and processes in the short, medium or even longer terms.

Because of the stringent requirements for qualification and certification a formal process for technology readiness and manufacturing readiness is followed.

The process for qualification, certification and industrialization as described in the ECHA EASA “elaboration” document is shown in **Figure 20**.

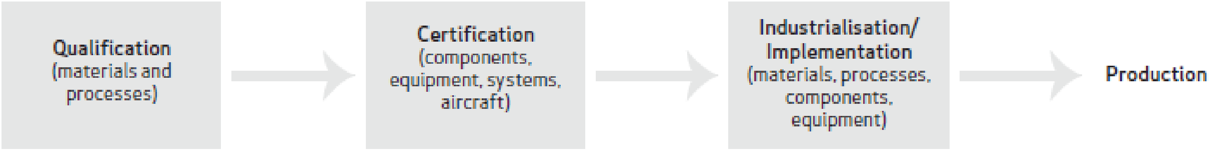


Figure 20: Illustration of the qualification, certification and industrialisation processes.

This diagram is perhaps overly simplified and doesn’t indicate the significant level of research and development work required prior to qualification as described in chapter 5.1.. As stated in the “elaboration” document “This process is an extensive internal approval process with many different steps from basic technology research up to technology demonstration in a lab environment.” The actual process followed by OEMs in the aerospace sector more closely follows the framework for TRLs and Manufacturing Readiness Levels (MRLs) originally developed by NASA. OEMs usually adapt this TRL/MRL approach resulting in individual versions which are considered proprietary and cannot be presented here. The NASA version is shown in **Table 7**.

Table 7: Technology Readiness Levels – Overview (US Department of Defence (DoD), 2011).

TRL#	Level Title	Description
1	Basic principles observed and reported	Lowest level of technology readiness. Scientific research begins to be translated into applied research and development (R&D). Examples might include paper studies of a technology’s basic properties.
2	Technology concept and/or application formulated	Invention begins. Once basic principles are observed, practical applications can be invented. Applications are speculative, and there may be no proof or detailed analysis to support the assumptions. Examples are limited to analytic studies.
3	Analytical and experimental critical function and/or characteristic proof-of-concept	Active R&D is initiated. This includes analytical studies and laboratory studies to physically validate the analytical predictions of separate elements of the technology. Examples include components that are not yet integrated or representative.

TRL#	Level Title	Description
4	Component and/or breadboard validation in laboratory environment	Basic technological components are integrated to establish that they will work together. This is relatively “low fidelity” compared with the eventual system. Examples include integration of “ad hoc” hardware in the laboratory.
5	Component and/or breadboard validation in relevant environment	Fidelity of breadboard technology increases significantly. The basic technological components are integrated with reasonably realistic supporting elements so they can be tested in a simulated environment. Examples include “high-fidelity” laboratory integration of components.
6	System / subsystem model or prototype demonstration in a relevant environment	Representative model or prototype system, which is well beyond that of TRL 5, is tested in a relevant environment. Represents a major step up in a technology’s demonstrated readiness. Examples include testing a prototype in a high-fidelity laboratory environment or in a simulated operational environment.
7	System prototype demonstration in an operational environment	Prototype near or at planned operational system. Represents a major step up from TRL 6 by requiring demonstration of an actual system prototype in an operational environment (e.g., in an aircraft, in a vehicle, or in space).
8	Actual system completed and qualified through test and demonstration	Technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development. Examples include developmental test and evaluation (DT&E) of the system in its intended weapon system to determine if it meets design specifications.
9	Actual system through successful mission operations	Actual application of the technology in its final form and under mission conditions, such as those encountered in operational test and evaluation (OT&E). Examples include using the system under operational mission conditions.

In general the TRL assessments guide engineers and management in deciding when a candidate alternative (be it a material or process) is ready to advance to the next level. Early in the process, technical experts establish basic criteria and deliverables required to proceed from one level to the next. As the technology matures, additional stakeholders become involved and the criteria are refined. As specific applications are targeted as initial implementation opportunities, design and certification requirements are added to the criteria. Many more factors have to be taken into account prior to making a decision about transition of technology or replacing a material. A formal gate review process has been established by some companies to control passage between certain levels in the process.

A similar set of guidelines MRLs exist for the management of manufacturing risk and technology transition process. MRLs were designed with a numbering system similar and complementary to TRLs and are also intended to provide a measurement scale and vocabulary to discuss maturity and risk. It is common for manufacturing readiness to be paced by technology or process readiness. Manufacturing processes require stable product technology and design. Many companies combine the aspects of TRLs and MRLs in their maturity assessment criteria as issues in either the technology or manufacturing development will determine production readiness and implementation of any new technology.

Referring back, now, to **Figure 20**, the general process steps can be loosely correlated to the steps in the TRL and MRL frameworks. Qualification begins after TRL 6 when technology readiness has been demonstrated. Certification begins around TRL 9 at the latest and may be performed in parallel with qualification. Industrialization/Implementation are not tracked on the NASA TRL scale, but some

OEMs refer to this phase as TRL 10. As previously stated, what is missing from the diagram, is the necessary and significant work that is performed before reaching technology readiness at TRL 6.

The following sections describe the highlights of the entire process from definition of needs before technology development begins through to implementation. The emphasis here is to provide a description of the general process while highlighting the inherent complexities.

One additional point to keep in mind when reviewing the process description that follows is that there is no guarantee that the initial process to identify an alternative for a substance is successful. Failure is possible at every stage of the TRL process. The impact of failure can be significant in terms of time.

5.1. Development and qualification

5.1.1. Requirements development

A need for a design change may be triggered due to many reasons. The one of interest here is when a substance currently used for production of aerospace parts are targeted for sunset (e.g. chromates). Completely removing one substance may impact various parts and systems on an aircraft or spacecraft and may involve many different processes with different performance requirements.

Once a substance is identified to be targeted by a regulation, a first step is to identify the materials and processes containing the specific substance. Most companies rely upon the information provided by the chemical manufacturer in the Safety Data Sheet (SDS). This information source has many limitations when used for substance identification including: lack of reporting due to protection of proprietary data; reporting large concentration bands to protect specific formulary data; different disclosure requirements based upon country (articles exemption, thresholds, de minimis, specific substance classifications, etc.) to name a few. After identifying the materials and processes and associating them with specifications and other design references parts get identified along with, applications and products potentially impacted. This is the first step in order to assess the impact for the company.

This work requires contributions from numerous personnel from various departments of an aerospace company like Materials & Processes, Research & Development, Engineering, Customers Service, Procurement, Manufacturing, Certification, including affiliates in other countries and Risk Sharing Partners.

Current production aircraft may have been designed 20 to 30 years ago (or more) using design methods, tools, and data that are not easily revisited. Industry standards may have been used as a starting point, but most OEMs refine these requirements for their specific needs and create their own proprietary specifications with substantiating data.. Changing the drawings implies the ability to assess the original design basis and data to determine what testing is required to demonstrate equivalent performance, which may not be possible when data, tools and test fixtures may be lost, or economically viable to expend a tremendous amount of design resources for out-of-production products.

Note: When a new design is needed e.g. to remove a substance, it may not be compatible with the existing one, this means that spare parts designs of the original materials/configurations may need to be preserved in order to be able to produce spare parts for the aircraft using the original (baseline) configuration. This is an additional impact to be taken into account.

Once a substitution project is launched, technical specialists, from engineering and manufacturing departments, must define the requirements that the alternatives have to fulfil.

Alternatives must satisfy numerous requirements. In many cases requirements are identified that introduce competing technical constraints and lead to complex test programmes. This can limit the evaluation of alternatives. For instance, for some materials, dozens of individual engineering requirements with similar quantities of industrial requirements may be defined.

Categories of technical requirements may include:

- Materials and processes requirements (e.g. corrosion resistance, adhesion strength),
- Design requirements (e.g. compatibility of the component's geometry complexity and with the coating application technique),
- Industrial requirements (e.g. robustness and repeatability),
- Environment, Health & Safety requirements.

Definition of needs itself can be complex and requires significant timeframe. The complexity can be due to:

- Different behaviour of the substitute compared to original product: new requirements may be defined. In this case, sufficient operational feedback to technically understand the phenomenon and reproduce it at laboratory scale is a must in order to be able to define acceptance criteria.
- Requirements may come from suppliers and have an impact on the design.
- Constraints from EHS regulations evolution.

Once initial technical requirements are defined, potential solutions can then be identified and tested. The timeframe for initial requirements development can last up to 6 months. Note that requirements may be added and continue to be refined during the different levels of maturity.

5.1.2. Technology development

The development process (typically TRL 4-6) is complex, and several years are often necessary before reaching development phase end (TRL 6). The following points explain why it may be long and complex:

- Developing solutions usually necessitates several testing phases before meeting the numerous requirements, which often induce several loops to adjust the formulation / design.
- Some tests are long lasting (e.g. some corrosion tests last 3000h or longer)
- In some cases, potential alternatives are patented, preventing multiple sources of supply, which is an obstacle to a large supply-chain deployment due to increases in legal costs and in some cases a reduction in profitability for the business.
- When no 1 to 1 replacement solution is available, each alternative process must individually be considered to determine for which specific quantitative application it is suitable. This work represents a significant resources mobilization, especially in term of drawings update and implementation of alternatives which due to the multiple work streams takes longer with higher costs. Moreover, spare parts and maintenance processes redesign may result in complex management both at the OEM and the Airlines. Additionally, substances regulations are evolving throughout the long research and development phase and life cycle of aircraft, which is another challenge for OEMs. There is a risk that significant investments could be made to develop and qualify alternative solutions involving substances with low EHS impacts identified at that point in time. Solutions may be developed and finally qualified, however, in the meantime, EHS constraints on those substances increased to a point where they now meet the SVHC criteria.

- When the suppliers have no “off the shelf” solutions, they have to develop new ones considering the list of requirements that are often highly complex to combine (see the description of requirements in the above paragraph).
- Drawings impact: The replacement of a material / process may impact the complete design of a part. Additionally, the mating part/counterpart functionality must be analysed too (materials compatibility, dimensional compatibility, stress compatibility). This may lead to redesign of the complete part plus mating parts.
- Process instructions shall be elaborated

The description of the development process is included in the qualification section of the ECHA EASA “elaboration” document. The text is reproduced here for continuity.

> “Qualification precedes certification and is the process under which an organisation determines that a material, process, component or equipment have met or exceeded specific performance requirements as documented in a technical standard or specification. These specifications, often abbreviated as spec(s), contain explicit performance requirements, test methods, acceptance testing, and other characteristics that are based upon the results of research, development and prior product experience.
>
> The industry relies upon standards issued by government-accredited bodies, industry or military organisations, or upon company-developed proprietary specs. Most materials and process specifications include either a “Qualified Products List” (QPL) or “Materials Control” section that identifies products that have met the requirements. Application and use of these qualified products must be assessed and certification implications addressed before being used on aircraft hardware.
>
> OEMs rely upon the expertise of the chemical formulators to provide viable candidates to test against specific material and process specs.”

It is important to note that many iterations of these formulas are rejected in the formulator’s laboratory and do not proceed to OEM evaluation. Formulators estimate 2 to 5 years before candidates are submitted to OEMs.

> “Once candidate(s) are developed, the OEM evaluates candidates by performing screening testing. If the candidate passes screening, testing is expanded to increase the likelihood that the preparation will pass qualification. If the candidate fails, which is often the case, material suppliers may choose to reformulate. It is not uncommon to iterate multiple times before a candidate passes screening. In some technically challenging areas, over 100 formulations have been tested with no success. This phase of development can take multiple years depending upon the material requirements. For those materials that pass screening, production scale-up, development of process control documents, manufacturing site qualifications, and extensive qualification testing is required to demonstrate equivalent or better performance to that which is being replaced. This phase of the process can also result in formulation or manufacturing iterations and may take several additional years. Depending on the complexity of the change and the criticality of the application (for example, fire protection or corrosion prevention have high safety implications and require development and testing against multiple, rigorous performance standards), re-certification may be required. The industry is ultimately limited by the material formulators’ willingness to expend their resources to develop alternative materials and technologies to be tested.”

The small volumes of materials sold, demanding performance requirements, and tightly controlled manufacturing processes for aviation customers provides insufficient incentive for reformulation in some cases. When material formulators are not willing to reformulate their materials new sources need to be sought.

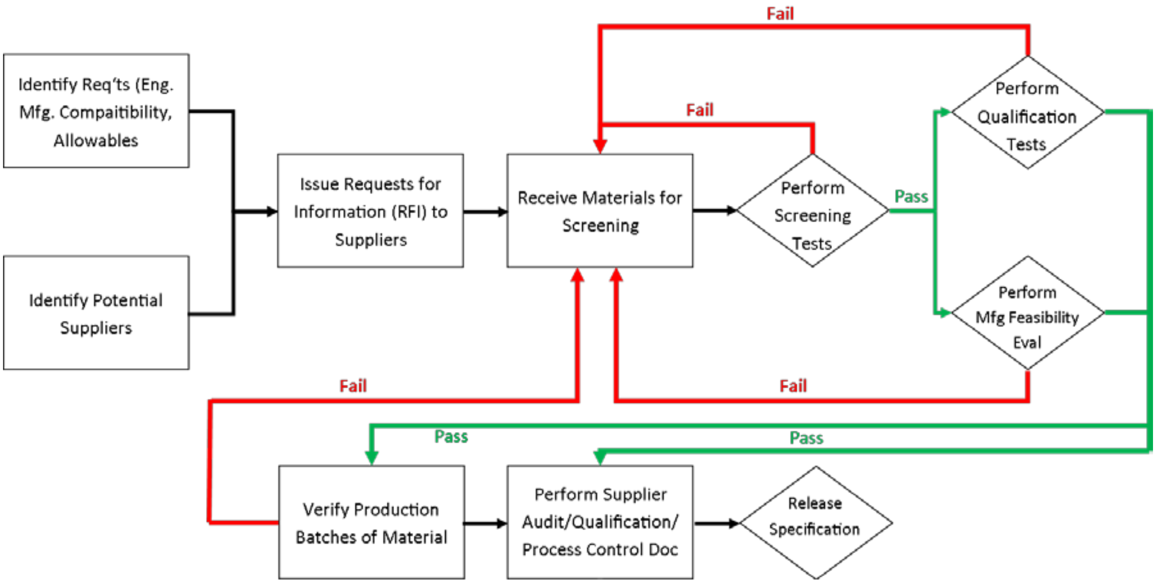


Figure 21: Illustration of the technology development and qualification process. (EASA, 2014, amended).

> "This process [TRL 1-6 development] is an extensive internal approval process with many different steps from basic technology research up to technology demonstration in a lab environment. Depending upon the difficulty of the technical requirements, these initial steps can easily take 3-5 years. After initial laboratory testing, each specific application must be reviewed, which means additional testing for specific applications / parts. Airworthiness Certification begins at this same time, this certification can take from 6 months to years. Additional time is needed for production scale-up and development of a supply chain."

It should be noted that the timeframes for development and qualification stated in the "elaboration" document have been combined and may be understated in the case of chromates. Depending on the application and the complexity of material and process requirements this process can easily take multiple years. As noted in the "elaboration" document the timeframe for development alone is typically a minimum of 3 to 5 years. Our experience with replacement of the substance addressed in this dossier is that the development takes much longer. For typically successful projects the duration is 3 to 5 years. For unsuccessful projects the development goes through repeated iterations and has taken over 30 years and still continues with limited success.

5.2. Qualification

Only after a technology has demonstrated technology readiness level 6, do the OEMs begin the qualification. All material, components, equipment or processes have to meet or exceed the specific performance requirements which are defined in the Certification Specifications documented in technical standards or specifications as described in chapter 5.3. These are issued by military organisations, government-accredited bodies, industries or upon company-developed proprietary specifications. Products which have met all requirements are included in the documents as "Qualified Products List" (QPL) or in the "Materials Control" section.

The main reasons for qualification are:

- To fulfil requirements by the Airworthiness Authorities European Aviation Safety Agency (EASA) and it is the first level of the Aircraft Certification Pyramid
- To ensure that only Approved, reliably performing Materials, Parts and Processes are used to produce Aircraft Components and Systems.

- To ensure that the product, the process or method is compliant with the Industry Regulations and Aircraft Manufacturer requirements to fulfil a specified function
- To provide a level of confidence and safety
- To ensure consistent quality of products and processes
- To ensure Supplier control, and to guarantee production and management system robustness, throughout the Supply Chain

The qualification process is mandatory to demonstrate compliance with airworthiness and certification requirements: the qualification process ensures that the technical and manufacturing requirements documented in the relevant material and/or process specifications are met. The qualification process comprises several steps before materials/processes are qualified. Even if most showstoppers are identified during the development phase, process confirmation/production verification are performed during the qualification phase. In case of failure product qualification will be cancelled and the development phase must start again from the beginning.

Based upon OEM experience, the time period needed to pass the qualification process is estimated to be on the order of 8 years and can be even longer when major test failures occur. This is one of the main challenges for chromates replacement. Depending upon the materials, processes and criticality of the applications being evaluated, in-service evaluation and monitoring will be required and can extend to 15 years or more depending upon application.

5.3. Certification

This next step is to certify, that an aircraft and every part of it complies with all applicable airworthiness regulations and associated Certification Specifications (specs). This step is also well described in the “elaboration” document and is reproduced here for continuity.

> “Certification is the process under which it is determined that an aircraft, engine, propeller or any other aircraft part or equipment comply with the safety, performance environmental (noise & emissions) and any other requirements contained in the applicable airworthiness regulations, like flammability, corrosion resistance etc.
>
> Although the airworthiness regulations (and associated Certification Specifications) do not specify materials or substances to be used, they set performance specifications to be met (e.g. fire testing protocols, loads to be sustained, damage tolerance, corrosion control, etc.). These performance specifications will drive the choice of substances to be used either directly in the aircraft or during the manufacturing and maintenance activities. Some examples of performance requirements are the following:
>
> - Resistance to deterioration (e.g. corrosion) Environmental damage (corrosion for metal, delamination for composites) and accidental damage during operation or maintenance.
> - Corrosive fluids - Hydraulic fluids; Blue water systems (toilet systems and areas); leakage of corrosive fluids/substances from cargo.
> - Microbiological growth in aircraft fuel tanks due to moisture/contamination in fuel cause severe corrosion. Such corrosion debris has the potential to dislodge from the fuel tanks, migrate through the fuel system, and lead to an in-flight engine shutdown.
> - Resistance to fire – Flammability Requirements Fire-proof and fire-resistance. Aircraft elements are expected to withstand fire for a specified time without producing toxic fumes; this leads to using products like flame retardants, insulation blankets, heat protection elements in hot areas (e.g. around engines).
>
> The primary certification of the aircraft (or engine and propeller) is granted to the manufacturer by the Competent Aviation Authority of the “State of Design” which is typically the authority of the state where the manufacturer of the aircraft (or engine or propeller) is officially located (EASA in the case

> of aircraft designed and manufactured in the EU and European Free Trade Association countries). Aircraft that are exported to other countries will have to be certified (validated) also by the authority of the "State of Registry".
>
> Manufacturers work with the certification authorities to develop a comprehensive plan to demonstrate that the aircraft meets the airworthiness requirements. This activity begins during the initial design phase and addresses the aircraft structure and all systems in normal and specific failure conditions (e.g. tire failure, failure of structural components, hydraulics, electrical or engines). The tests needed to demonstrate compliance, range from thousands of coupon tests of materials, parts and components of the airplane, up to tests that include the complete aircraft or represents the complete aircraft (system). The performance and durability of the various materials have to be confirmed while the behaviour of the parts, components and the complete airplane will have to be tested in the applicable environmental and flight conditions including various potential damage or failure conditions. For a new Type Certificate this overall compliance demonstration covers several thousands of individual test plans of which some will require several years to complete. Often, after the initial issuance of the Type Certificate, the tests that have the objective to demonstrate durability of the aircraft during its service life, will continue.
>
> All the different aspects covered by the Type Certificate together define the "approved type design" which includes, among other aspects, all the materials and processes used during manufacturing and maintenance activities. Each individual aircraft has to be produced and maintained in conformity with this approved type design.
>
> Changes to the approved type design may be driven by product improvements, improved manufacturing processes, new regulations (including those such as new authorisation requirements under REACH), customer options or the need to perform certain repairs. When new materials or design changes are introduced, the original compliance demonstration will have to be reviewed for applicability and validity, in addition to a review of potential new aspects of the new material or design change that could affect the airworthiness of the aircraft. Depending on the change, this review could be restricted to coupon or component tests, but for other changes this could involve rather extensive testing. E.g. changes in protective coatings could affect not only the corrosion resistance but could also affect the friction characteristics of moving components in actuators in the different environmental conditions, changing the dynamic behaviour of the system, which in the end affects the dynamic response of the airplane.
>
> Before the new material or design change can be introduced on the aircraft, all test and compliance demonstrations have to be successfully completed and approved by the Competent Authority. This approval results in the issuance of a Supplemental Type Certificate (STC), change approval or repair approval.
>
> It is important to note that, according to the EU Regulation No 216/2008, EASA is the design competent authority for civil aircraft only. Any other aircraft (e.g. military, fire-fighting, state and police aircraft) will have to follow similar rules of the corresponding State of Registry.
>
> To be able to maintain and operate an aircraft the responsible organisations must be approved by the competent authority and compliance is verified on a regular basis. Maintenance of an aircraft requires that the organization complies with specific procedures and materials described in the maintenance manuals which are issued by and the responsibility of the OEMs."

As noted in the "elaboration" document, in optimal cases certification can take as little as 6 months but typically will take several years. The duration really depends on the specific material and application.

5.4. Implementation / industrialisation

An aircraft consists of several million parts which are provided by thousands of suppliers or manufactured internally by OEMs. Significant investment, worker training and manufacturing documentation may be required to adapt the manufacturing processes which sometimes require changes in existing facilities or the construction of new facilities.

The industrial implementation is usually scheduled to follow a step wise approach to minimize the technical risks and benefit from lessons learned. This implies that the replacement is not implemented in one shot in all plants and at all suppliers but stepwise. Each OEM may own several plants, e.g. up to 20 manufacturing sites / final assembly lines worldwide for some of them.

Furthermore, the implementation of an alternative process may induce new development and modification in the complete process flow.

The following text is reproduced from the “elaboration” document and describes the process for implementation of an alternative:

> “Industrialisation is an extensive step-by-step methodology followed in order to implement a qualified material or process throughout the manufacturing, supply chain and maintenance operations, leading to the final certification of the aerospace product. This includes re-negotiation with suppliers, investment in process implementation and final audit in order to qualify the processor to the qualified process.
>
> Taking into account that an aircraft is assembled from several million parts provided by several thousand suppliers, this provides an indication of the complexity for the industrialisation stage of replacement materials/processes, and the supply chain which provides these parts.
>
> Special challenges are:
>
> - Low volumes limit influence on changes to suppliers’ materials / processes
> - Procurement & insertion of new equipment
> - Scale-up & certification of new process
> - Incompatibility of coatings could be a risk.
> - Re-negotiation of long term agreements with suppliers*.
> - Increased complexity of repairs – Multiple different solutions for different applications as a substitute for a single, robust process. For example, currently all aluminium parts can be repaired with one chromated conversion coating. In some specific cases, the future state could require different conversion coatings for each aluminium alloy and application environment. Since different alloys are not easily distinguishable on the shop floor, ensuring that the proper repair procedures are used will be much more difficult. If alternate means of compliance approvals are requested for repair facilities or airlines, regulatory agencies are unlikely to have adequate knowledge or technical data to make informed assessments.
>
> The operating environment, longevity of the aircraft, supply chain complexity, performance and above all airworthiness requirements are some of the considerations which can constrain the ability of the industry to make changes and adopt substitutes in the short, medium or long term.”

*Changes to the design or manufacturing may require re-negotiations with suppliers which can be time-consuming, especially when long-term contracts are concerned. The supply chain is complex in the aviation industry; it includes but is not limited to chemical manufacturers, importers, distributors, formulators, component manufacturers, OEMs, Airline operators, and aftermarket repair and overhaul activities.

The timeframe for implementation and industrialisation is unknown. Simple changes may take 18 months to 5 years. Our experience with replacement of the substance addressed in this dossier is that full implementation and industrialization has yet to be accomplished. Implementation by airlines and MROs further requires that an alternative is approved by the OEM and made available in the maintenance documents.

When the alternative process is included in the maintenance documents, challenges described above have to be faced out by airlines and MRO to implement the alternative. Here, for operating supplies and testing time frames, another 3 years might be necessary, depending on complexity of the alternative. When more alternative processes have to be established simultaneously, as it is currently the case for tartaric-sulphuric acid anodizing (TSA) and boric-sulfuric acid anodizing (BSA), more than 5 years might be necessary to fully implement the alternatives.

It is important to note that the implementation/industrialization step ('TRL10') refers to the whole supply chain. This includes external as well as internal industrialization. In case a suitable chrome free alternative is developed in the future, it needs to be implemented across a vast and complicated supply chain, which in turn is time and cost intensive requiring significant additional investment in new machinery and plant on the part of existing suppliers. Additionally, any substitution is linked to major resourcing exercises at new suppliers with the capabilities of industrialising the application of the new products or processes. The switch-off of one production process and the belonging supply chain without validating and qualifying the new alternative process and corresponding supply chain is not feasible.

The development and approval process is illustrated in **Figure 22**.

5.5. Examples

In 2003, RoHS (Directive on Restriction of Hazardous Substances, 2002/95/EC) was adopted by the EU and took effect on July 2006. This directive triggered companies to substitute lead-based solder in electronic assemblies and all subsequent changes in the product designs and manufacturing processes: Basic research was started in the example company in 2003 with the selection and tests of alternative lead-free solder. The Research Program is still running in 2014 and the qualification and industrialization phase is ongoing: Components (IC’s, connectors, printed circuit boards etc.) had to be changed due to the higher soldering temperature that all materials have to withstand with lead-free solder and most of the manufacturing equipment had to be replaced by new ones. This fundamental replacement of lead (Pb) for aerospace and military applications with harsh environmental conditions will take more than 15 years in total to be deployed up to TRL9.

Work on a replacement for chromic acid anodizing (CAA) began in 1982. The initial driver for this R&D effort was to reduce emissions of Cr(VI) and comply with federal and local clean air regulations. Initial requirements were identified and four candidate solutions were evaluated. One candidate solution was down selected in 1984. Qualification testing began in 1985. A process specification for BSA was released in 1990. In 1991 and 1992 industrialization began as several Boeing facilities began producing parts using the BSA process. One outside supplier also began processing parts to the Boeing specification in 1992. Evaluation of additional applications continued into the mid-1990s. In 2015, industrialization of the BSA alternative for CAA is still not complete. Many Boeing suppliers are shared with other OEMs and industries impeding the conversion to BSA from CAA because they must continue to support multiple customer requirements. Note that for unprimed parts a dilute chromate seal is still required to provide required stand-alone corrosion resistance. Work is ongoing to develop alternatives for this process. It is also worth noting that boric acid is now being proposed for Annex XIV requiring authorization. Should this happen alternatives may need to be developed for BSA. Other OEM solutions may need to be evaluated, qualified and certified.
Both examples are illustrated in **Figure 22** compared to the overall development process as outlined above.

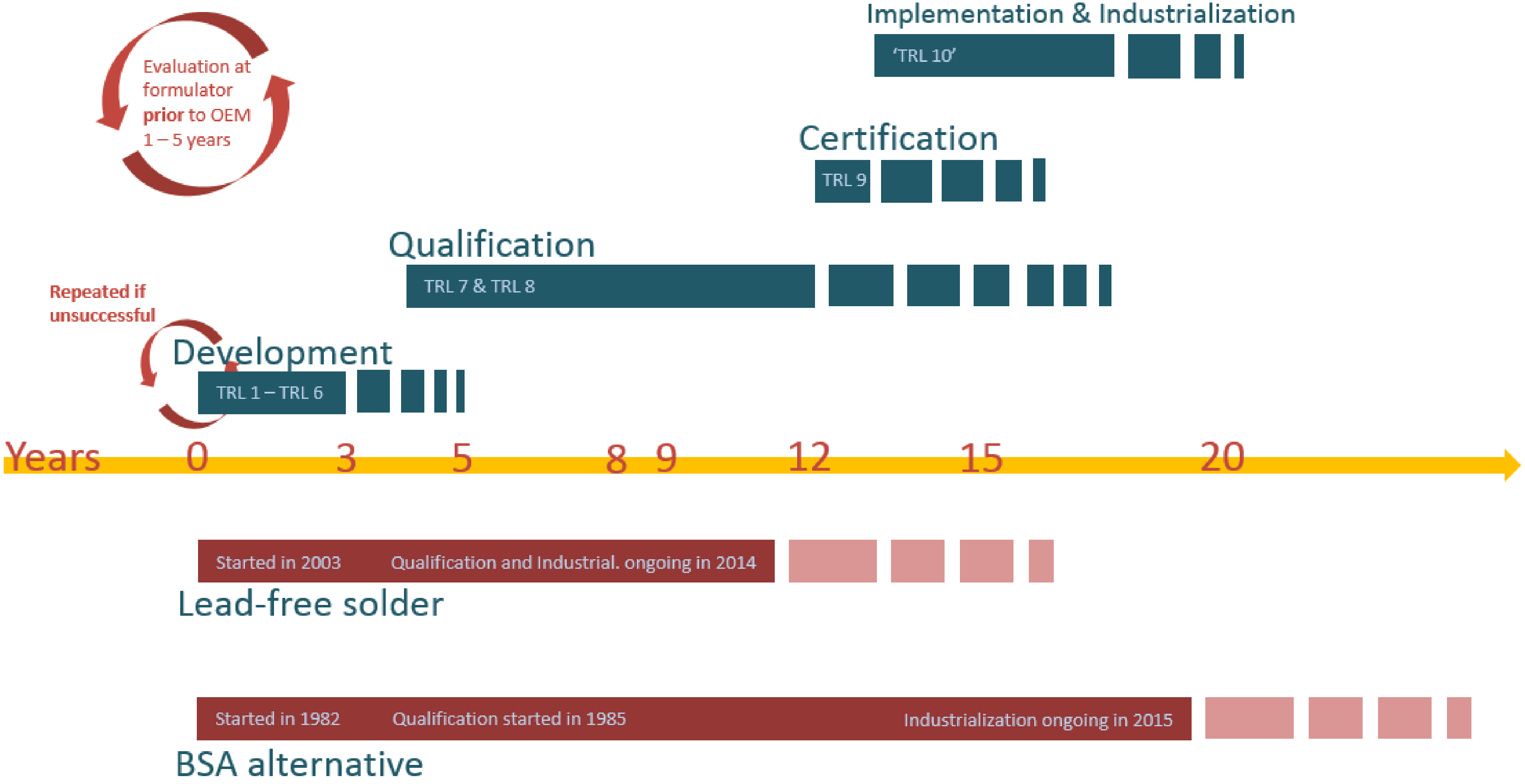


Figure 22: Development and approval process in the aerospace sector. Examples from previous implementations are included. Loops indicate potentially iterative steps due to unsuccessful evaluation at the formulator or unsuccessful development.

6. IDENTIFICATION OF POSSIBLE ALTERNATIVES

6.1. Description of efforts made to identify possible alternatives

To prepare for the authorisation of 8 Chromium VI Compounds, the industry consortium CCST (Miscellaneous Chromium VI Compounds for Surface Treatment REACH Authorisation Consortium) of comprising 28 members, was launched in 2012.

The aim of CCST was to efficiently gather and analyse all necessary information for the three pillars of the authorisation dossier (CSR, AoA, SEA).

6.1.1. Research and development

As mentioned earlier in this document, a large amount of research over the last few decades has been commissioned to identify and develop viable alternatives to Cr(VI). The unique functionalities of Cr(VI) (explained in detail in chapter 3.5) make it challenging and complex to replace the substance in surface treatment applications where superior corrosion or adhesion properties are required to ensure safe performance in a demanding environment. Numerous research programmes were conducted funded by Europe clean sky (MASSPS, ROPCAS, LISA, DOCT, MUST, MULTIPROJECT) as well as programmes funded by United States Air Force (USAF) or other national funded programmes (e.g. LATEST in UK). Some key research programmes are listed below.

Amongst a number of initiatives in that respect, the Airbus Chromate-Free (ACF) project was launched more than 10 years ago with the aim to progressively develop new environmental friendly Cr(VI)-free alternatives to qualified products and processes used in aircraft production and maintenance. Even prior to the launch of ACF, R&D efforts included the objective to remove Cr(VI) compounds use. The ACF project is organised into several topics for the different fields of technologies concerned by the replacement. ACF specially addressed applications where chromates are used in production or applied to the aircraft; such as CAA, basic primer, and external paints. In addition, bonding primer, pickling, Cr(VI)-based chemical conversion coatings, passivation of stainless steels, passivation of metallic coatings or alternatives to hard chromium are included in the remit of this project. A similar initiative was set up for spacecraft, the Launcher chromate-free (LCF) project.

In 2006, Boeing in cooperation with the DoD started a three-year program called “Environmentally Benign Coating System for Department of Defense Substrates” for the development of new Cr(VI)-free coating systems, based on rare-earth conversion coatings.

Industry is not only working on one-to-one replacements for Cr(VI) applications but also reconsidering whole current coating systems. The large investment in innovative coating technologies may lead successively to a paradigm shift within the next few decades.

As an example, the HITEA (Highly Innovative Technology Enablers for Aerospace) project was initiated in 2012; a 17-member consortium consisting of aerospace OEMs, suppliers, paint application companies and academics with the goal to identify and evaluate suitable alternative systems. In 2014, the tested alternatives are planned to reach TRL2. After the initial phase, the project will focus on a handful of promising alternatives, where further testing will be undertaken within the next years and completion of the research project is planned for 2015. Qualification (TRL6) will take up to 5-8 years from now. In 2008, the multi-company project SOL-GREEN was initiated for the development of protective coatings of Al/Mg alloys (Cerda et al, 2011). Since these coatings solutions are not based on electrochemical conversion, and so require a complete change in technical approach, the industrial production qualification is expected not before 2025. Phase 1 was finished last year, showing that SOL-GREEN 1 faces some technical issues. Therefore, the main objective of SOL-GREEN 2 is to assess and develop an electrophoresis process to apply the anti-corrosion coatings using a SOL-GEL technique for complex geometry parts. These challenges are currently ongoing and the research is mainly conducted at laboratory scale (TRL2) at universities and in some partner’s plants. However, as mentioned above, this is a long term solution (10-15 years).

For high performance surfaces in demanding environments, the use of Cr(VI)-containing primer systems is essential to ensure safety of the aircraft over the lifetime of the component. As illustrated in **Figure 13**, there are various steps within the multilayer coating system. These include pre-treatment processes for adequate preparation of the substrate for subsequently applied layers. It is of greatest importance, that the combination of pre-treatments, primer and topcoat leads to a well-prepared multilayer system providing all necessary key requirements for the respective applications as described in detail in chapter 3.2. The use of Cr(VI) is crucial to ensure highest quality and to meet the requirements of the aerospace industry. Current developments for coating systems incorporate at least one layer of Cr(VI). Complete non-Cr(VI) coating systems are currently under evaluation.

At a first glance, available performance data for some Cr(VI)-free corrosion inhibitors provided in the alternative assessment in chapter 0 indicate interesting results in laboratory scale. However, one has to note that the materials mostly have been tested individually and not as part of a complete coating system. When selecting an alternative, the performance of the material has to be evaluated as part of a whole system, which is a complex and stepwise development process as described in chapter 5. In many cases, this level of evaluation will require component/system-level testing unless field-testing data exists on the exact coating system, substrate, and application (AMMTIAC, 2012).

On the basis of the aforementioned unique properties and diverse functionalities of Cr(VI), the multilayer coating systems, where alternatives have to be identified and implemented into all layers to be completely Cr(VI)-free, and the extensive and promising research already made, one-to-one solutions or innovative technics are not expected to be finally implemented within the next 15 years.

6.1.2. Data searches

For the analysis of alternatives, extensive literature and test reports were provided by the technical experts of the consortia members. Furthermore, searches for publically available documents were conducted to ensure that all potential alternate processes to Cr(VI)-containing applications were considered in the data analysis.

In addition to databases for scientific literature, the following programmes were intensively consulted: Toxics Use Reduction Institute, Massachusetts, US (www.turi.org/); The Advanced Materials, Manufacturing, and Testing Information Analysis Center (AMMTIAC) (http://ammtiac.alionscience.com/).

Searches for SDS for Cr(VI)-containing and Cr(VI)-free applications were also conducted.

Based on these data, primary scoping led to the development of a generic questionnaire containing potential alternatives to Cr(VI)-based coating systems. As a result of this, additional alternate processes, mentioned by companies from the aerospace sector were included in the initial list of Alternatives, which can be found in Appendix 2.

6.1.3. Consultations

A questionnaire was provided to all consortia members to get an overview of and experience with the alternatives, completeness and prioritisation of critical parameters for their specific processes and the minimum technical requirements.

During this survey, additional alternatives have been identified which were included into the aforementioned initial list. At this stage of the data analysis, several alternatives had been screened out after bilateral discussions with the companies, based on confirmation that they might be general alternatives to Cr(VI)-based processes (e.g. for functional chrome plating), but are not applicable for the use defined here.

To verify data and obtain more detailed quantitative information, further focused technical questionnaires were sent out and discussed with the consortia members. In addition, site visits to selected companies were carried. These were carefully chosen to adequately represent the different uses, industry sectors, countries and the size of companies. Discussions with technical experts followed by a final data analysis led to the formation of a list of alternatives divided into 3 categories, according to their potential to be suitable for the specific use.

The most promising alternatives within this use (category 1 and 2) are assessed in detail in the following chapter, the Category 3 alternatives, which are not applicable for the here defined use are summarised in Appendix 2.

6.2. List of possible alternatives

The alternatives are classified according to their relevance; as Category 1 (focus of CCST members, relevant R&D on these substances ongoing) or Category 2 (discussed mainly in literature, clear technical limitations, may only be suitable for other industry sectors or for niche applications but not as general alternative). Category 3 alternatives, which are not applicable for the use defined here, are summarised in Appendix 2.

An overview of the potential alternatives in each process is provided in **Table 8**, below.

Table 8: List of alternatives categorised.

Matrix/Process	Cr(VI)-free corrosion inhibitors	Application
Epoxy/polyurethane (PU)-based primers with Cr(VI)-free inhibitors	Cr(VI)-free inhibitors (confidential) (Category 1)	BA, BO
	Calcium-based corrosion inhibitors‡ (Category 1)	BA, BO
	Organic corrosion inhibitors like 5-methyl-1H-benzotriazol (Category 2)	BA
	Phosphate-based corrosion inhibitors ‡ (Category 1)	BA, BO
	Magnesium-based corrosion inhibitors ‡ (Category 1)	BA, SP
	Molybdate-based corrosion inhibitors‡ (Category 2)	BA, BO
	Rare earth-based corrosion inhibitors ‡ (Category 2)	BA, BO
	Zinc-based inhibitors‡ (Category 2)	BA
Electrocoat primer technology	Various ‡ (Category 2)	BA, SP

Silane-based processes including Sol-gel coatings	Sol-gel coatings ‡ (Category 1)	BA, BO, SP
BA (Basic primer); BO (Bonding primer); SP (structural primer) ‡ only some substances in this group may be considered possible alternatives;		

7. SUITABILITY AND AVAILABILITY OF POSSIBLE ALTERNATIVES

The aerospace industry uses Cr(VI)-based primers to inhibit corrosion of metallic structures (aluminium alloys and other lightweight materials). In addition to their corrosion-inhibiting properties, Cr(VI)-based coatings provide excellent adhesion to the both the metal substrate and subsequent coatings. In general, these systems consist of an active corrosion inhibiting agent (pigment) and a binding agent. These compounds are embedded into a matrix system such as synthetic resin. Thus, the performance of a primer system is not only dependent on the corrosion inhibiting properties of the pigment itself, but rather on the complex interaction between pigment and matrix.

This complex interplay was taken into account when assessing the potential alternatives to currently used Cr(VI) coating systems. Therefore, in the dossier different “types” of alternatives were assessed. Potential corrosion inhibiting agents or complete primer systems based on these substances were identified and evaluated with regard to their specific properties to fulfil standard requirements from the respective industry sector. If one substance showed promising results in the laboratory test, data from further testing were evaluated (if available), where the substance was incorporated into a matrix system and standard tests were performed.

Moreover, this dossier covers different matrix systems. In addition to general data (relating to inherent properties of the matrix used in primer systems), also - more importantly - data from complete primer systems which are developmental systems or partly commercially available were taken into account. This included systems where the specific composition was confidential business information and the corrosion inhibiting substance was not known.

CATEGORY 1 ALTERNATIVES: The alternatives assessed in this chapter are considered the most promising, where considerable R&D efforts have been carried out within the aerospace sector. Category 1 alternatives were often discussed during the consultation phase; most data on Cr(VI)-free primer/paint systems was provided on these substances. In most cases, they are in early research stages and still showed technical deficiencies when it comes to the demanding requirements from the aerospace sector, such as corrosion performance. However, some of these replacement substances may already be qualified and used in other industry sectors or for niche applications within aerospace but not as a general alternative to Cr(VI) containing coating systems.

CATEGORY 2 ALTERNATIVES: The alternatives assessed in this chapter are mainly discussed in literature and were rarely mentioned during the consultation phase. In most cases, they are in very early research stages and showed clear technical limitations when it comes to the demanding requirements from the aerospace sector.

For the assessment of the feasibility of the alternatives, summarizing overview tables with a colour coding were included in the dossier.

The colours are as follows:

- Red: not sufficient - the parameters/assessment criteria do not fulfil the requirements of the respective sector.
- Green: sufficient - the parameters/assessment criteria do fulfil the requirements of the respective sector.
- Yellow – the parameters/assessment criteria fulfil some requirements for some but not all applications/sectors (only used for the assessment of the technical feasibility)

7.1 Epoxy/PU-based primers with Cr(VI)-free inhibitors

In general, primer systems consist of an active corrosion inhibiting agent, a binding agent/matrix system (e.g. epoxy, polyurethane), a catalyst and a thinner as described in chapter 3.2. Thus, the performance of a primer system is not only dependent on the corrosion inhibiting properties of the pigment itself, but rather on the complex interaction between pigment and matrix.

This complex interplay was taken into account when assessing the potential alternatives to currently used Cr(VI) coating systems. Here, data from complete primer systems was taken into account which are partly commercially available. For other systems the specific composition was confidential business information and the corrosion inhibiting substance was not disclosed.

Epoxy resins constitute a class of reactive low molecular weight pre-polymers or higher molecular weight polymers which normally contain at least two epoxide groups. The epoxy content of these resins is an important characteristic and is commonly expressed as either epoxide number (the number of epoxide equivalents in 1 kg of resin (Eq./kg)) or as the equivalent weight (the weight in grams of resin containing 1 mole equivalent of epoxide (g/mol)). To enhance their mechanical and chemical properties, epoxy resins may undergo the process of curing: cross-linking with themselves or with a wide range of co-reactants including polyfunctional amines, acids, phenols, alcohols, and thiols. This leads to a change in material properties, such as high temperature resistance and chemical resistance. It is also possible to use these aromatic epoxy resins in a mixture with aliphatic epoxy resins. In particular epoxy resins derived from polyoxypropylene glycol can be used to promote the elasticity of the binders.

Epoxy/PU-based matrix systems can be used for bonding and basic primers that can be applied on several substrates. Bonding and basic primer coatings are used on titanium, titanium alloys, aluminium, aluminium alloys and steel parts. In addition, epoxy/PU-based basic primers are applied on composite and stainless steel parts.

7.1.1 Cr(VI)-free inhibitors (confidential)

7.1.1.1 Substance ID and properties

In this chapter, data is derived from primer systems where the matrix system used is known but the composition was confidential business information (CBI) and the specific corrosion inhibiting substance was not disclosed.

General information on properties of matrix compounds as well as the overall risk for human health and environment is provided within Appendix 3.1.1

7.1.1.2 Technical feasibility

<u>Use in basic primers</u>

Corrosion resistance: Performance of various Cr(VI)-free inhibitors (CBI) was tested in epoxy and PU matrix as basic primers. In laboratory tests, corrosion performance was promising with no corrosion pits on AA2024-T3 pre-treated with TSA after 3000 h in the salt spray test (ISO 9227 and ISO 7253). The maximum filament length in the filiform corrosion test (EN3665) was 2 mm after 960 h. Long term testing is necessary to investigate the corrosion performance of these formulations in detail (3000-9000 h (ISO 9227); 3000-6000 h (ISO 7253)).

When tested on alloys pre-treated with chromate-free conversion coatings and subsequent epoxy or PU primer application, performance was clearly not sufficient: creepage > 1.25 mm was visible on the substrate in the salt spray test (ISO 9227 and ISO 7523) after 3000 h, and the filament length was > 2 mm after 960 h in the filiform corrosion test (EN3665).Thus, the overall minimum corrosion requirements of the aerospace sector reported during the consultation were not met.

The tested system did not provid active corrosion inhibition, as tarnishment with aluminium hydroxide appeared after 1000 hours inside the scratch.

Other parameters: With regard to adhesion, chemical resistance and compatibility with the substrate sufficient performance results were achieved.

Summary and overview of the conclusion regarding feasibility of Epoxy/PU-based basic primer systems with Cr(VI)-free inhibitors				
(Long-term) Corrosion resistance	Adhesion	Chemical resistance	Compatibility with substrate	Active corrosion resistance
Depending on pre-treatment and substrate	🟩	🟩	🟩	🟥

Use in bonding primers

Corrosion resistance: Performance of various Cr(VI)-free inhibitors (CBI) was tested in an epoxy matrix for bonding primer applications. In laboratory tests, corrosion performance was promising with no corrosion pits on AA2024-T3 pre-treated with TSA after 3000 h in the salt spray test (ISO 9227 and ISO 7253). The maximum filament length in the filiform corrosion test (EN3665) was 2 mm after 960 h. Long term testing is necessary to investigate the corrosion performance of these formulations in detail (3000-9000 h (ISO 9227); 3000-6000 h (ISO 7253)).

When tested on alloys pre-treated with Cr(VI)-free conversion coatings and subsequent primer application, performance was clearly not sufficient: creepage > 1.25 mm was visible on the substrate in the salt spray test (ISO 9227 and ISO 7523) after 3000 h, and the filament length was > 2 mm after 960 h in the filiform corrosion test (EN3665). Thus, the overall minimum corrosion requirements of the aerospace sector reported during the consultation were not met.

The tested system did not provid active corrosion inhibition, as tarnishment with aluminium hydroxide appeared after 1000 hours inside the scratch.

Other parameters: With regard to adhesion, chemical resistance and compatibility with the substrate sufficient performance results were achieved.

Another specific commercial product identified by the aerospace sector is the water-based, one-part, non-chromate epoxy bonding primer. It could be a serious alternative considering most of requirements are met, however, remaining requirements including industrial up scaling and compatibility shall still be validated

Summary and overview of the conclusion regarding feasibility of Epoxy/PU-based bonding primer systems with Cr(VI)-free inhibitors				
(Long-term) Corrosion resistance	Adhesion	Chemical resistance	Compatibility with substrate	Active corrosion resistance
Depending on pre-treatment and substrate	🟩	🟩	🟩	🟥

7.1.1.3 Economic feasibility

Against the background of significant technical failure of these alternate systems, no detailed analysis of economic feasibility was conducted. However, based on the literature research and consultations there is no indication that the discussed alternative is not economically feasible.

7.1.1.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances and products reported during consultation were reviewed for comparison of the hazard profile. Please note that the exact substance identity and composition of products used is not known as this is confidential business information of suppliers. Since no detailed analysis for a complete epoxy/PU-based formulation could be carried out given the insufficient information, the reduction of overall risk cannot be assessed.

7.1.1.5 Availability

Many R&D programs are ongoing, especially in the USA and Europe. The most important available information comes from the USA where research on Cr(VI)-free alternatives was launched a long time ago, under the leadership of the DoD in order to provide the military with Cr(VI) alternatives. Several alternatives are available on the market that are qualified, mainly for the military sector or for some very specific applications. A Cr(VI)-free PU-primer is qualified for military aircraft, but not for structural applications. Cr(VI)-free PU-topcoats (self-priming topcoats) are subject to flight testing on many C-17 aircraft. Even if these products meet various military specifications, they do not necessarily fulfil the requirements of the civil aviation industry.

It is understood that some companies, currently have Cr(VI)-free epoxy-based bonding primers in qualification phase. A development program that includes mechanical tests on coupons and OEM articles is planned on a steel substrate. The implementation program will start in 2014 and will take approximately 4 years for first applications on steel. For other substrates, as the most important high copper containing Al alloy, significantly more time will be necessary before first replacement bonding primer will enter the implementation phase. Here, most optimistic estimates account for 8 years if all testing passes with no need to reformulate new candidates. More likely, multiple iterations and testing of multiple candidates have to be carried out until successful replacements for key applications. Altogether, passing all TRL stages up to deployment of newly developed bonding primer formulations will require at least 8-15 years.

In the aerospace sector, primer/paint manufacturers confirmed that R&D regarding Epoxy/PU primers containing Cr(VI)-free inhibitors for the replacement of basic primer applications is ongoing. So far, none of the companies have succeeded in developing a system which is sufficient with regard to the demanding requirements of the aerospace industry, especially with respect to (long-term) corrosion. During the consultation it was stated that if successful identification of a primer formulation containing Cr(VI)-free inhibitors in laboratory scale is achieved, the additional time required for product validation on laboratory scale is >1 year, provided all required tests are passed successfully. Thereafter, the formulation would be proposed for testing at OEM, where 3-5 years may be necessary until the substance would enter qualification phase (refer to chapter 5.1). Altogether, in a best case scenario (i.e. no major drawbacks occur), passing all TRL stages up to deployment of newly developed compounds will require at least 15 years.

7.1.1.6 Conclusion on suitability and availability for epoxy/PU-based primers with Cr(VI)-free inhibitors

For **bonding primer applications**, some Cr(VI)-free epoxy/PU-based alternatives are available on the market. These primers are stated to show equivalent performance with regard to standard corrosion testing, adhesion coefficient of friction, and are partly compatibility with substrates. R&D is advanced for steel substrates, where the implementation phase is about to start for bonding primers. For other substrates, Al alloys being the most important substrate for the aerospace sector, further time is necessary until the implementation program will start.

In summary, these systems showed promising results as alternative to bonding primer containing strontium chromate, and are currently in advanced R&D phase for several substrates. First implementations may be expected within the next 5-7 years on steel. For other substrates, this process will take even longer. As a consequence, for a full implementation of bonding primer alternatives on all substrates plus for MRO applications, at least 8-15 years will be necessary.

For **basic primer applications** several developmental products based on Epoxy/PU-matrices have been tested on Al alloys. Their performance with regard to corrosion is not sufficient to comply with the overall minimum requirements of the aerospace sector, especially with regard to extended corrosion. During the consultation, further R&D in very early laboratory scale was reported.

In summary, these systems are technically not equivalent to Cr(VI)-based products and are therefore not a general alternative to basic primer applications including strontium chromate. According to the current very early stage of research, at least 15 years after a viable candidate is developed would be necessary until implementation of the alternative products into the supply chain.

7.1.2 Calcium-based corrosion inhibitors

7.1.2.1 Substance ID and properties

Several calcium-based inhibitors are available on the market. The exact substance identity and composition of primers is not known as this is confidential business information of suppliers.

General information on properties of calcium compounds as well as the overall risk for human health and environment is provided within Appendix 3.1.2.

7.1.2.2 Technical feasibility

Corrosion resistance: Information provided by aerospace formulators indicated that several calcium compounds have been tested. The results clearly showed that calcium carbonate, calcium hydroxide, calcium metasilicate and calcium borosilicate perform insufficiently with regard to the minimum corrosion requirements in SST (ISO 9227) and FFT (EN 6556).

In addition to information provided during the consultation, corrosion performance results of products containing calcium-based inhibitors are publically available. In general, most of these products are tested on steel plates, so their corrosion performance cannot be easily transferred to high strength Al alloys which are used in aerospace, marine, automotive and other applications. Various calcium-containing formulations were tested according to ASTM 117 and ISO 9227. Importantly, they were not tested as standalone inhibitors, but in combination with several other compounds such as magnesium, molybdenum and phosphates.

Adhesion: Taking the adhesion requirements into account, these products showed insufficient performance for aerospace applications. It is not known, if these issues are linked to the inhibitors or the matrix. Further testing results on different parameters and different substrates like Al alloys are currently not available for these products. As no in-depth experience with these compounds exists within the aerospace sector, further R&D including tests on component and aircraft level would be required before considering these substances as potential alternatives.

Only one company from the aerospace sector reported ongoing research at laboratory scale. As during the consultation almost no experience with these alternatives was provided and planned R&D activities are very limited, the relevance of calcium compounds alone or in combination with other substances is questionable.

Summary and overview of the conclusion regarding feasibility of epoxy/PU-based primer containing calcium compounds as corrosion inhibitors	
Corrosion resistance	Adhesion
🟥	🟥

7.1.2.3 Economic feasibility

Against the background of significant technical failure of these alternate systems, no detailed analysis of economic feasibility was conducted. However, based on the literature research and consultations there is no indication that the discussed alternative is not economically feasible.

7.1.2.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances and products reported during consultation were reviewed for comparison of the hazard profile. Based on available information on four strictly confidential calcium-based inhibitors used within this alternative (See Appendix 3.1.2), they are in best case not classified. In worst case the substances are classified as Eye Dam. 1, Skin Irrit. 2, STOT SE 3, Skin Corr. 1B, Eye Irrit. 2A, Resp. Sens. 1A. Calcium-based primers are also available on the market. Classification and labelling (SDS) of these products is not publically available. However, transition from strontium chromate – which is a non-threshold carcinogen – to one of these inhibitors/products would constitute a shift to less hazardous substances.

7.1.2.5 Availability

Calcium-containing primer formulations are available on the market. However, these formulations show clearly inferior performance with regard to corrosion and/or adhesion properties. In addition, public information on performance is only available for steel substrates, not for aluminium or other substrates.

During the consultation, it was reported that R&D efforts are at very early laboratory scale with primer/paint systems including calcium compounds. Additional time will be required to identify suitable calcium-containing products for the replacement of strontium chromate-based primer/paint systems. To date, it is not known if calcium compounds will be used as standalone within newly developed primer formulations or, more likely, the research will focus on a combined approach, with calcium being one of several inhibiting compounds within a formulation. If successful identification of an inhibitor occurs at laboratory scale, the additional time required for product validation at laboratory scale is >1 year, provided all required tests are passed successfully. Thereafter, the formulation would be proposed for testing at OEM, where 3-5 years may be necessary until the substance could enter qualification phase (refer to chapter 5.1). Altogether, in a best case scenario, for passing all TRL stages up to deployment of a newly developed compound at least 15 years after a viable candidate is developed are necessary, if no major drawbacks occur.

In summary, the relevance of calcium alone or in combination with other substances as inhibiting agent in primer/paint formulations is questionable.

7.1.2.6 Conclusion on suitability and availability for calcium-based corrosion inhibitors

Several development products containing calcium compounds as standalone or in combination with other inhibiting agents have been tested on steel with little data on Al alloys. All of them failed to meet the minimum corrosion requirements of the aerospace industry already at laboratory scale. Some calcium-based inhibitors are available on the market. Their performance on steel with regard to corrosion and/or adhesion is not sufficient to comply with the overall minimum requirements of the aerospace sector, especially with regard to extended corrosion. During the consultation, R&D at very early laboratory scale was reported.

In summary, Ca-based primer/paint systems are technically not equivalent to Cr(VI)-based products and are therefore not a general alternative. It is questionable, if these systems will qualify for further R&D efforts within the aerospace sector, since other substances seem to be more promising. For substitution of strontium chromate in basic or bonding primer applications at least 15 years after a viable candidate is developed would be necessary until implementation of the alternative products into the supply chain.

7.1.3 Organic corrosion inhibitors like 5-methyl-1H-benzotriazol

7.1.3.1 Substance ID and properties

In the presence of organic inhibitors, both anodic and cathodic corrosion prevention is sometimes observed. More importantly, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors are usually designated as 'film-forming', protecting the metal by forming a hydrophobic film on the metal surface. It is understood that organic inhibitors are adsorbed according to their ionic charge and the charge on the surface (Klechka, 2001). Several organic corrosion inhibitors have been tested by industry. The identity of the active substances in most compounds are subject to strict confidentiality (CBI).

In the aerospace sector benzotriazol (BZT) derivatives, e.g. 5-methyl-1H-benzotriazol (5-BZT) are under investigation as corrosion inhibitors for use in (epoxy) basic primers and coatings on Al alloys, that contain specific percentages of e.g. magnesium, manganese, zinc and copper. Other interesting candidates are organo-zinc pigments, which are currently subject to R&D at many formulator facilities. A summary of information on properties, hazard classification and labelling of BZT is given in Appendix 3.1.3.

7.1.3.2 Technical feasibility

Use in basic primers

BZT and derivates (e.g. 5-BZT): These substances are part of extensive R&D efforts in several industry sectors.

Corrosion resistance: As mentioned during the consultation, one of the most important performance parameters is corrosion resistance. The following results are obtained during the EU-funded research project LISA (light-weight low-cost surface protection for advanced aircraft structures). The operating mechanisms of appropriate corrosion inhibitors for aluminum alloys (AA2024) can be separated into two basic “inhibition principles”: (i) the formation of protective layers on cathodic sites and (ii) the stabilization of the matrix Al oxide. As standalone inhibitors (not in a paint matrix), BZT and BZT in combination with Na_2HPO_4 was shown to ensure those functionalities at laboratory scale. However, apart from demonstrating sufficient performance in solution, for “real-life applications” inhibitors need to perform satisfactorily when brought into the primer/paint matrix (IFAM, 2006).

Tests results from end-users in the aerospace sector demonstrate that the release of BZT corrosion inhibitors from the primer/paint matrix is hindered (no active corrosion inhibition), thus resulting in failing standard corrosion tests when applied on aluminium alloys. Furthermore, BZT as inhibitor in primer/paint matrix showed blisters on the surface of the substrates due to osmotic effects.

Another important function of Cr(VI) as corrosion inhibitor is their buffer capacity, preventing the decrease of the pH value (= acidification) on aluminium surfaces by catching protons released upon aluminium contact with water: $Al + 2\ H_2O \rightarrow Al(OH)_3 + H^+$. Indeed, the stable range of Al is between pH 3 and pH 9, while Cr(VI)-based inhibitors buffer in the range of pH 5.5 to 7.5. Therefore, the pH value of an inhibitor in the primer/paint system as well as its buffer capacity are important factors for corrosion inhibition. However, for BZTs the pH-stabilizing effect is still to be evaluated (IFAM, 2006).

Different corrosion results were obtained by formulators for a formulation with 5-BZT in epoxy basic primers on aluminium alloys (AA2024-T3 pre-treated with TSA anodising or Cr(VI)-free conversion coatings). Corrosion protection was sufficient in the filiform test after 960 h, but was not in line with the requirements in salt spray tests according to ISO 9227 and ISO 7523 (3000-6000 h). Here, corrosion pitting appears after 2000 h and creepage is within the range of 2 mm. Furthermore, it was shown that the diffusion process is efficient within 168 h of salt spray exposure (test according to ISO 9227). However, after 168 h exposure corrosion pitting was observed in the scratch.

Chemical resistance: Tests results (ISO 1518, ISO 2409 and ISO 2812) from formulators on chemical resistance of 5-BZT in epoxy basic primers on aluminium alloys (AA2024-T3 pre-treated with TSA anodising, chromate conversion coatings or Cr(VI)-free passivation demonstrated sufficient chemical resistance after water immersion for 14 days and 1000 h immersion at 70°C in hydraulic fluid (grade 0 to 1 in both tests).

In contrast, tests conducted with BZT as inhibitor in primer/paint matrix failed the hydraulic fluid and water resistance tests, indicating insufficient chemical resistance when applied on Al alloys. Apart from that, nitrogen chemically contained in the BZT inhibitors may take part in the curing process of the primer /paint matrix, where it will be consumed or interferes with the curing process. Consequently the paint matrix is negatively influenced, leading to blistering in water exposure and missing resistance to hydraulic fluids (IFAM, 2006).

Other parameters: Moreover, tests according to ISO 2409 conducted by formulators with the above mentioned primer-substrate combination proved good adhesion properties and sufficient compatibility with substrate as results were GT0 for dry adhesion.

Other organic compounds: It was reported during the consultation that several organic substances have been tested by paint manufacturers. However, the inhibitors have been kept confidential.

Corrosion resistance: The corrosion performance of these tested inhibitors was clearly insufficient (ISO 9227, ISO 7253). With particular regard to active corrosion inhibition, these alternatives were clearly inferior to chromate containing primers/paints, providing less or no active corrosion inhibition compared to Cr(VI)-based products (no or insufficient diffusion process from related matrices).

Therefore, these formulations containing organic corrosion inhibitors cannot be used in applications that presuppose active corrosion inhibition.

Stability: Paint manufacturers consistently reported that all organic substances that have been tested in basic primers for use on aluminium alloys revealed stability issues. Further studies on the stability of these substances have to be carried out.

Other parameters: Moreover, laboratory tests according to ISO 2409 conducted by formulators showed sufficient adhesion properties, chemical resistance and compatibility with substrate.

In addition to information provided by the aerospace industry, performance results of commercially available formulations with organic corrosion inhibitors will be presented here. In general, the majority of these products are tested on steel plates, so their corrosion performance cannot be easily transferred to high strength Al alloys which are used in aerospace, marine, automotive and other applications. It should be stated that the tested organic corrosion inhibitors incorporated in different matrices do not fulfil the minimum requirements for the aerospace sector. Tests according to ASTM B 117 and ISO 9227 showed clear signs of corrosion and/or blistering after 192-600 h on different steel substrates. One system demonstrated an improved performance where only slight corrosion after 2218 h on bare aluminium was detected (9:1 combination of zinc calcium strontium aluminium orthophosphate silicate hydrate and zinc-5-nitroisophthalate in solvent borne acid cured epoxy DTM (direct-to-metal) coating). However, these results are still not sufficient with regard to the corrosion requirements of the aerospace sector (≥ 3000 h) as reported during the consultation. Further performance data on different parameters and different substrates such as Al alloys are not available for these products.

Primer/paint systems - Summary and overview of the conclusion regarding feasibility of Epoxy/PU-based primer containing organic corrosion inhibitors				
(Active) corrosion resistance	Adhesion	Chemical resistance	Stability	Compatibility with substrate
🟥	🟩	🟩	🟥	🟩

7.1.3.3 Economic feasibility

Against the background that these systems are currently no general alternative, no detailed analysis of economic feasibility was conducted. However, based on the literature research and consultations there is no indication that the discussed alternative is not economically feasible.

7.1.3.4 Reduction of overall risk due to transition to the alternative

As the alternative is not a general technical alternative, only classification and labelling information of substances and products reported during the consultation were reviewed for comparison of the hazard profile. Based on the available information on the substances used within this alternative (see Appendix 3.1.3), in best case inhibitors/products are not classified. As worst case they are classified as Skin Corr. 1B/1C, Eye Dam. 1, STOT SE 3, Acute Tox. 4, Aquatic Acute 1 and/or Aquatic Chronic 1. As such, transition from strontium chromate – which is a non-threshold carcinogen – to one of these inhibitors/products would constitute a shift to less hazardous substances.

7.1.3.5 Availability

For use as an inhibitor in **basic or bonding primer**, further R&D is ongoing in the aerospace sector as well as by paint/primer formulators. If suitable combinations of BZTs with other inhibitors are found in laboratory tests for primer/paint applications, functionalities and performance must be further investigated by end-users in the aeronautic sector in extended tests in addition to the known standard tests to simulate real-life conditions. Currently, products are in early development stage and have not yet entered TRL-phase.

7.1.3.6 Conclusion on suitability and availability for organic corrosion inhibitors

In summary, BZT will never be a standalone replacement for Cr(VI) for primer systems because it does not have all the functionalities required by the specifications of the aerospace sector. The corrosion performance of the tested BZT derivates does not meet the requirements from industry, in addition to other requirements such as stability, or chemical resistance. The available alternative primer systems containing organic corrosion inhibitors are technically not feasible for aerospace applications. As these alternatives have not yet reached the TRL-phase at OEMs, at least 15 years after a viable candidate is developed are necessary until industrialisation will be complete.

7.1.4 Phosphate-based corrosion inhibitors

7.1.4.1 Substance ID and properties

Since the decline in the use of lead and chromate containing anti-corrosive pigments on toxicological and ecological grounds, the importance of phosphate containing pigments has grown. As they still cannot replace the traditional Cr(VI) containing anti-corrosive pigments in every respect, efforts are being made to improve both their effectiveness (by combining various phosphates or by adding other substances such as zinc oxide or zinc borate), and their reactivity. Some of the most important members of this group include orthophosphates and polyphosphates, zinc phosphate, aluminium triphosphate, barium phosphate and aluminium zinc phosphate. Polyphosphates are amongst the technically most promising Cr(VI)-free anticorrosive inhibitors where high performance protection is required (ECHA, Annex XV Dossier, 2011). Phosphate produces a surface layer on the applied substrate which provides a measure of corrosion protection.

Several phosphate-based inhibitors are under R&D at primer/paint manufacturers. The exact substance identity and composition in primers is not known as this is confidential business information of suppliers. General information on the properties of relevant phosphate based corrosion inhibitors and the overall risk for human health and environment is provided within Appendix 3.1.4.

7.1.4.2 Technical feasibility

General assessment: Products including inhibitors such as aminophosphate salts of magnesium, mixtures of aminophosphate salts of magnesium and calcium in solvent or water based epoxy primers, and modified orthophosphate or polyphosphate corrosion inhibitors are commercially available. These can be used in primers on steel, galvanised steel and aluminium for the painting of trucks, buses and agricultural vehicles. During the consultation, aerospace industry stated that commercially available products only meet current specifications for applications on “exterior schemes”, meaning their performance is not sufficient for basic or bonding primer applications.

R&D for the aerospace sector is ongoing in the field of phosphate-based corrosion inhibitors. During the consultation, primer/paint manufacturers consistently reported a large variety of different phosphate-based substances that are or have been included in R&D programs (preferentially on aluminium alloys). However, none of the companies succeeded in developing a phosphate-based primer/paint system which is sufficient with regard to the demanding requirements of the aerospace industry.

Corrosion resistance: Aminophosphate salts of magnesium/calcium in solvent or water-based epoxy primers and primers with modified orthophosphate or polyphosphate corrosion inhibitors give clearly insufficient corrosion resistance results. In detail, they failed to meet the aerospace requirements for basic and bonding primer in the salt spray test (ISO 7253), filiform corrosion test (EN 3667) and alternating immersion-emersion test (EN 3212) on aluminium (3000-6000 h, max. 1.5 mm (ISO 7253) and <960 h. max. 2 mm corrosion from scratch (EN 3665), >1500 h max 1.25 mm from scratch (EN 3212), respectively).

Formulators tested various inhibitors in amine or epoxy matrices as well as in combination with zinc phosphate and cerium salt. Again, the minimum requirements of the aerospace sector (3000-9000 h in ISO 9227 and up to >> 6000 h in ISO 7253) are not met regarding corrosion resistance: after 3000 h on Al substrates pre-treated with Cr(VI)-free conversion coatings and on TSA pitting corrosion appeared, creepage from scratch was >1.25 mm and around 1.5 mm, respectively. Results from a filiform corrosion test confirmed that 960 h may be achieved. If companies require increased performance in tests according to EN 3665, ISO 9227 and/or ISO 7253, phosphate-based corrosion inhibitors do not constitute technically suitable alternatives. In addition, all tested phosphate-based corrosion inhibitors do not show active corrosion inhibition.

Publically available information on inhibitors based on Mg/Ca-aminophosphate salts in solvent or water-based epoxy primers demonstrates that the corrosion performance of these products is also not sufficient on steel. Significant corrosion is observed after 288-430 h in the salt spray test.

Adhesion: Adhesion properties can be met for basic primers and paints in applications on aluminium alloy AA2024-T3 pre-treated with TSA or conversion coatings (GT0 for dry adhesion, and GT0-1 after water immersion for 14 days).

Chemical resistance: Observed chemical resistance of phosphate-based corrosion inhibiting agents in basic primers and paints on aluminium alloy AA2024-T3 pre-treated with TSA or conversion coatings is in line with the aerospace companies’ minimum requirements.

Other parameters: In addition, the latter alternatives provide equal performance for bonding applications with regard to layer thickness (2-12 µm), coefficient of friction and compatibility with substrate.

In addition to research and development products, it was reported that a water-based chromate-free epoxy-based bonding primer containing aluminium metaphosphate is available on the market. It is an alternative bonding primer for use on several metals and alloys (titanium, titanium alloys, aluminium, aluminium alloys, steel and stainless steel). Its standard corrosion performance is stated to be only equal to strontium chromate in bonding primers for specific space applications where corrosion resistance requirements are lower than for the main processes within the aerospace sector. Furthermore, no information on long-term corrosion performance is available. Like all phosphate-based corrosion inhibitors, this inhibitor does not provide active corrosion inhibition. The paint adhesion is equal to strontium chromate in bonding primers (ISO 2409: GT ≤ 1).

Furthermore, publicly available performance results of phosphate-based inhibitors (modified orthophosphates and polyphosphates) marketed by two companies will be presented here.

In general, the majority of these products are tested on steel plates, so their corrosion performance cannot be easily transferred to high strength Al alloys which are used in aerospace, marine, automotive and other applications. On steel plates, the results from the salt spray tests according to ASTM B 117 and ISO 9227 with orthophosphate-based systems (modified with zinc, magnesium or molybdenum) indicate inferior protection of the substrate, with corrosion appearing after 550-860 h. On bare aluminium, the organically modified zinc orthophosphate hydrate in epoxy matrix showed significantly better performance than zinc phosphate. These results are still not sufficient with regard to the corrosion requirements of the aerospace sector (≥ 3000 h) reported during the consultation. The industry polyphosphate-based products show first signs of corrosion after 550-1400h in salt spray tests (ASTM B 117, ISO 9227) when applied on cold rolled steel panels (ST 1205).

In addition, information is provided on primers designed for high performance coatings (primarily in coil) and aircraft epoxy primers based on strontium polyphosphate. They show less corrosion and blistering compared to a control when applied on hot dipped galvanised steel pre-treated with a Cr(VI)-free bonder after 3360 h in salt spray tests (ASTM B 117, ISO 9227). However, after 3360 h, reduced adhesion to the substrate can be observed, as blistering occurred with both inhibitors. Taking the adhesion requirements from the aerospace industry into account (GT0 under dry conditions), these primers show insufficient performance for aerospace applications. Further testing results on different parameters and different substrates like Al alloys are currently not available for these products. As no in-depth experience with these alternatives exists within the aerospace sector, further R&D including tests on component and aircraft level is required before considering these substances as potential alternatives.

A general issue for the safety and performance of an aircraft is the presence of microorganisms in turbine engine fuels, which can be found in free water at the junction of the water and fuel in a fuel tank. These microorganisms can not only interfere with the proper functioning of filter elements, but also provide a medium for electrolytic corrosion in contact with the fuel tank surface (Federal Aviation Administration, 2012). Since uptake of phosphates will promote microbial growth it may be necessary to add additional substances to the primer system (or to the fuel, if necessary) to prevent enhanced microbial growth when using phosphate-based coating systems. According to data provided, fungal growth was not inhibited with a commercially available phosphate-based systems. Current investigations on fuel tank primer are in TRL 2.

Summary and overview of the conclusion regarding feasibility of epoxy/PU-based primer containing Phosphate-based corrosion inhibitors					
Corrosion resistance	Inhibition of fungal growth	Adhesion	Layer thickness	Chemical resistance	Compatibility with substrate
🟥	🟥	🟩	🟩	🟩	🟩

7.1.4.3 Economic feasibility

Against the background of significant technical failure of these alternate systems, no detailed analysis of economic feasibility was conducted. However, based on the literature research and consultations there is no indication that the discussed alternative is not economically feasible.

7.1.4.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances and products reported during the consultation were reviewed for comparison of the hazard profile. However, please note that the exact substance identity and composition of products containing phosphate-based corrosion inhibitors in primers is very often not known as this is confidential business information of suppliers. In a best case inhibitors/products are not classified. In a worst case they are classified as Skin Irrit. 2, Eye Dam. 1, STOT SE 3, Aquatic Acute 1, Aquatic Chronic 1, Acute Tox. 4. As such, transition from strontium chromate – which is a non-threshold carcinogen – to one of the above mentioned alternative inhibitors/products would constitute a shift to less hazardous substances.

7.1.4.5 Availability

Some phosphate-based alternatives for application on metals are available on the market that are considered to provide sufficient performance on trucks, buses and agricultural vehicles, but not for use in the aerospace sector. Furthermore, relatively new products are commercially available which are considered to provide improved performance on steel substrates compared to control samples or older standard products. However, publicly available test results refer to the performance of these inhibitors on steel substrates and the main substrate used in the aerospace sector is aluminium.

Research and development for the aerospace sector is ongoing in the field of phosphate-based corrosion inhibitors. Primer/paint manufacturers report a large variety of different phosphate-based substances that are or have been included in R&D programs (testing preferentially on aluminium alloys). However, none of the companies has succeeded in developing a phosphate-based primer/paint system which is sufficient with regard to the demanding requirements of the aerospace industry, particularly with respect to (long-term) corrosion. During the consultation a paint/primer manufacturer stated that if successful identification of a phosphate-based inhibitor occurs at laboratory scale, the additional time required for product validation at laboratory scale is >1 year, provided all required tests are passed successfully. Thereafter, the formulation would be proposed for testing at OEM, where 3-5 years may be necessary before the substance would enter qualification phase (refer to chapter 5.1). Altogether, in a best case scenario, passing all TRL stages up to deployment for a newly developed compound would take at least 15 years after a viable candidate is developed, if no major drawbacks occur.

7.1.4.6 Conclusion on suitability and availability for phosphate-based corrosion inhibitors

For some industry sectors, Cr(VI)-free phosphate-based primer/paint systems are already qualified and industrialised and provide sufficient performance on steel for the use in trucks, buses and agricultural vehicles. In the aerospace sector, they are part of extensive R&D efforts. Two inhibitors are available on the market which are stated to be designed for application in high performance coatings primarily in coils and aircraft primers. To date, none of these on-market systems are qualified for aerospace applications due to their insufficient performance with regard to corrosion resistance. In particular, no detailed information on long term testing under relevant environmental test conditions is currently available. At laboratory scale, some primers showed acceptable performance with regard to adhesion properties, layer thickness or chemical resistance. From a technical point of view, these systems are in early development stage in the aerospace industry.

In summary, phosphate-based primer/paint systems are technically not equivalent to Cr(VI)-based products and are therefore not a general alternative. For substitution of strontium chromate in basic or bonding primer applications a period of at least 15 years after a viable candidate is developed is anticipated until implementation of the alternative products into the supply chain.

7.1.5 Magnesium-based corrosion inhibitors

7.1.5.1 Substance ID and properties

Several magnesium-based inhibitors are available on the market. The exact substance identity and composition in primers is not known as this is confidential business information of suppliers.

General information on properties of relevant magnesium-based inhibitor systems as well as the overall risk for human health and environment is provided within Appendix 3.1.5.

7.1.5.2 Technical feasibility

Mg compounds as corrosion inhibitors in formulations are evaluated as replacement for Basic primer or structural primer.

Basic primer

Corrosion resistance: During the consultation, it was reported that different magnesium containing formulations were tested on aluminium alloy AA2024-T3 and Al alloys pre-treated with TSA or conversion coatings. The minimum corrosion resistance could not be fulfilled: the test results clearly indicate insufficient saltspray performance with corrosion occurring after 1000 h (ISO 7253, ISO 9227). When testing filiform corrosion (EN3665) the performance was in line with the specifications (960 h). The tested magnesium compounds do not provide active corrosion inhibition to the substrate.

Other parameters: It was stated that these formulations containing magnesium compounds in one basic primer fulfil the minimum requirements for adhesion, compatibility with substrate (GT0 for dry adhesion), and chemical resistance.

In addition to information provided during the consultation, performance results of magnesium containing formulations which are commercially available are presented below. On steel plates, the results from the salt spray test according to ASTM B 117 and ISO 9227 (with orthophosphate-based systems modified with an electrochemical active magnesium compound) indicate inferior protection of the substrate, with corrosion appearing after 550 h. Further test results on different parameters and different substrates like Al alloys are not available for these products.

Summary and overview of the conclusion regarding feasibility of epoxy/PU-based primer containing Mg-compounds as corrosion inhibitors				
Corrosion resistance	Adhesion	Active corrosion inhibition	Compatibility with substrate	Chemical resistance
🟥	🟩	🟥	🟩	🟩

Structural primer

Corrosion resistance: Specific performance results were provided for a sacrificial Mg-rich epoxy primer. This alternative meets the corrosion protection requirements for filiform corrosion (EN 3665, 960 h) but not in the salt spray test (ISO 9227 >3000 h): after 2000 h, water blisters (= adhesion loss of the coating) were detected. Furthermore, problems with active corrosion inhibition were encountered on anodized aluminium substrates. In addition, no tests have yet been performed to assess long-term corrosion protection and performance under service-life conditions.

Adhesion: The sacrificial Mg-rich epoxy primer passes the cross cut test (GT0). Basic primer alternatives show slightly reduced performance.

Compatibility with substrates: As stated during the consultation, the aerospace industry examined a Mg-rich epoxy primer for its compatibility with different substrates as an alternative for military specification (MIL-PRF-23377 Class N), which is used in corrosion resistant paint applications. The range of substrates used in the aerospace sector includes the following: aluminium alloys and steels and titanium alloys and CRES. When parts are assembled (secondary requirement), primer may be applied on additional substrates such as thermoplastic and thermoset composites. The tested alternative is qualified for painting of military aircraft exteriors in MRO applications. Mg-rich primers only function correctly with selective pre-treatments, as they must have electrical contact with the base metal. Conversion coatings act as a dielectric and electrically isolate the primer. Furthermore, they do not fulfil the requirements due to poor compatibility with anodised layers. Mg-rich epoxy primers are not qualified yet for application in production processes of OEMs.

Other parameters: Sacrificial Mg-rich epoxy primers can be used with different top-coats; during the consultation, it was reported that these primers generate immaculate surfaces (visual inspections) and provide sufficient hardness (scratch resistance > 1500 g in ISO 1518). In addition, curing at room temperature (processing temperature) is possible and the product is applicable on the whole aircraft.

It should be stated that, while the detailed composition of these formulation is not known, the sacrificial Mg primer contains “VOC exempt solvents” (halogenated hydrocarbons) which may not comply with national law (e.g. in Germany the BImSchV) or EU regulation.

Summary and overview of the conclusion regarding feasibility of Mg rich primer					
Corrosion resistance	Adhesion	Active corrosion inhibition	Free of VOC exempt solvents	Chemical resistance	Compatibility with substrate
🟥	🟩	🟥	🟥	🟩	🟥

7.1.5.3 Economic feasibility

Against the background of significant technical failure of these alternate systems, no detailed analysis of economic feasibility was conducted. However, based on the literature research and consultations there is no indication that the discussed alternative is not economically feasible.

7.1.5.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances and products reported during the consultation were reviewed for comparison of the hazard profile. Based on the available information on two strictly confidential magnesium-based inhibitors, they are in best case not classified. In the worst case scenario, the substances are classified as Skin Irrit. 2, Eye Irrit. 2 and STOT SE 3. The sacrificial Mg-rich primer is classified as Flam. Liq. 3, Skin Irrit. 2, Eye Irrit. 2, Skin Sens. 1, Aquatic Chronic 2, Acute Tox. 4, Asp. Tox. 1. As such, transition from strontium chromate – which is a non-threshold carcinogen – to one of these inhibitors/products would constitute a shift to less hazardous substances.

7.1.5.5 Availability

One magnesium containing formulation is available on the market; a zinc-free anticorrosive which is based on a calcium phosphate complex modified with an electrochemical active magnesium compound. Information on performance is only available for steel substrates, not for aluminium or other substrates with high relevance for the aerospace sector.

During the consultation, it was reported that R&D efforts are at very early laboratory scale with primer/paint systems including magnesium compounds. Additional time will be required to identify suitable magnesium-containing formulations for the replacement of strontium chromate-based basic or bonding primer systems. To date it is not known whether magnesium compounds will be used as alone within newly developed primer formulations or, more likely, research will focus on a combined approach, with magnesium being one of several inhibiting compounds within a formulation. If successful identification of an inhibitor occurs at laboratory scale, the additional time required for product validation on laboratory scale is >1 year, provided all required tests are passed successfully. Thereafter, the formulation would be proposed for testing at OEM, where 3-5 years may be necessary until the substance could enter qualification phase (refer to chapter 5.1). Altogether, in a best case scenario, for passing all TRL stages until deployment of newly developed compounds at least 15 years are necessary, if no major drawbacks occur.

In summary, the relevance of magnesium alone or in combination with other substances as inhibiting agent in primer/paint formulations is questionable.

7.1.5.6 Conclusion on suitability and availability for magnesium-based corrosion inhibitors

Several development products containing magnesium compounds as standalone or in combination with other inhibiting agents have been tested on Al alloys by paint manufacturers. All of them failed to meet the minimum corrosion requirements of the aerospace industry already at laboratory scale. During the consultation, R&D in very early laboratory scale was reported.

In summary, magnesium-based primer/paint systems are technically not equivalent to Cr(VI)-based products and are therefore not a general alternative. It is questionable, if these systems will qualify for further R&D efforts within the aerospace sector, since other substances seem to be more promising. According to the current very early stage of research, for substitution of strontium chromate in basic or bonding primer applications at least 15 years after a viable candidate is developed would be necessary until implementation of the alternative products into the supply chain.

7.1.6 Molybdate-based corrosion inhibitors

7.1.6.1 Substance ID and properties

The coating industry had used molybdate-based corrosion inhibitors (e.g. zinc molybdate, calcium zinc molybdate) since the early 1970s. Molybdate-based corrosion inhibitors and paints have different fields of application. While the soluble sodium molybdate is used to protect steel, aluminium and copper in central heating systems and automobile engine coolants, the insoluble compounds zinc molybdate, calcium molybdate, strontium molybdate and molybdenum orange (lead molybdate plus lead chromate phosphomolybdates) are used in paints, plastics, rubber and ceramics. Further application fields of molybdate corrosion inhibitors include water-based hydraulic systems and automobile engine anti-freeze. A range of molybdate corrosion inhibitors are commercially available and are for example used in acrylic and emulsion primers.

The corrosion inhibiting function of molybdate compounds in aqueous solution is based on a passivation process: the molybdate ions interact with the metallic substrate to promote the formation of an adherent oxide layer which inhibits the corrosion of the underlying metal substrate. Molybdates can also be used as complexing agents that inhibit copper in Cu-containing aluminium alloys.

Substance IDs and the risk to human health and the environment are summarised in Appendix 3.1.6 for substances where information was publically available. In addition, three strictly confidential molybdate compounds are regarded as potential alternatives. Their substance IDs and physicochemical properties are not presented within these tables.

7.1.6.2 Technical feasibility

Corrosion resistance: Formulators stated during the consultation that they have tested various molybdate-based corrosion inhibitors in solution and on different aluminium alloys. The corrosion performance in the salt spray test and the filiform test was clearly not sufficient, especially with regard to long-term corrosion requirements. These primers are suitable for trucks or buses but not for aerospace applications. Molybdenum containing primer/paint systems used on aluminium alloys showed clearly insufficient corrosion protection in SST, FFT and Alternate Immersion Emersion testing (AIE, corrosion pitting exceeding the maximum acceptable distance after 1000-3000 h, duration depending on the test). It was highlighted that molybdates do not provide self-sealing characteristics. According to one company from the aerospace sector, this substance does not even function as an anticorrosive agent unless mixed with strong oxidising agents.

Other parameters: These inhibitors passed requirements for hardness (min. 1500g, ISO 1518), adhesion (GT0, ISO 2409), layer thickness (dry film thickness 15-25 µm, ISO 2808), and impact resistance (degree > 2, ISO 6272). Testing on chemical resistance against water and hydraulic fluid (ISO 2409, ISO 1518) showed that molybdenum containing primer/paint systems do not meet the requirements from the aerospace sector. Due to these negative results, no further testing on these primers is expected by OEMs from the aerospace industry.

In addition to the alternatives named by formulators during the consultation, molybdate-based alternatives are available on the market; results of corrosion performance on steel but not on aluminium alloys are publicly available. The inhibitor zinc molybdenum orthophosphate hydrate in water borne acrylic primer is advertised to show good corrosion results when applied in water-based coating systems using 1-part polyurethanes. When applied on cold rolled steel panels (ST 1205) almost no corrosion is seen in SST (ASTM B 117-11) after 864 h. The inhibitor zinc aluminium molybdenum orthophosphate hydrate in combination with a water borne alkyl emulsion primer is advertised to be comparable in performance to Cr(VI) containing systems in a variety of applications. In a test according to ASTM B117-11 for use on cold rolled steel panels (ST 1205), however, corrosion is clearly visible after 672 h.

<table>
<tr><th colspan="5">Summary and overview of the conclusion regarding feasibility of epoxy/PU-based primer containing molybdenum compounds as corrosion inhibitor</th></tr>
<tr><td>Corrosion resistance</td><td>Adhesion</td><td>Layer thickness</td><td>Chemical resistance</td><td>Hardness</td></tr>
<tr><td>🟥</td><td>🟩</td><td>🟩</td><td>🟥</td><td>🟩</td></tr>
</table>

7.1.6.3 Economic feasibility

Against the background of significant technical failure of these alternate systems, no detailed analysis of economic feasibility was conducted. However, based on the literature research and consultations there is no indication that the discussed alternative is not economically feasible.

7.1.6.4 Availability

Molybdate-containing primer formulations are available on the market. However, these formulations show clearly inferior performance with regard to corrosion and chemical resistance. They may be sufficient on steel for use in trucks or buses, but not for aerospace applications.

During the consultation, it was reported that few R&D with primer/paint systems based on molybdate-compounds is ongoing at paint manufactures at very early laboratory scale. Additional time will be required to identify suitable molybdate-containing products for the replacement of strontium chromate-based primer/paint systems. To date it is not known if molybdate compounds will be used as standalone within newly developed primer formulations or, more likely, research will focus on a combined approach, with molybdate being one of several inhibiting compounds within a formulation.

If successful identification of an inhibitor at laboratory scale occurs, the additional time required for product validation on laboratory scale is >1 year, provided all required tests are passed successfully. Thereafter, the formulation would be proposed for testing at OEM, where 3-5 years may be necessary until the substance could enter qualification phase (refer to chapter 5.1). Altogether, in a best case scenario, for passing all TRL stages until deployment of newly developed compounds at least 15 years after a viable candidate is developed are necessary, if no major drawbacks occur.

In summary, the relevance of molybdate alone or in combination with other substances as inhibiting agent in primer/paint formulations is questionable.

7.1.6.5 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances and products reported during the consultation were reviewed for comparison of the hazard profile. Zinc molybdate is classified as Skin. Irrit. 2, Eye Irrit. 2 and STOT SE 3. In addition to zinc molybdate, three strictly confidential substances were reported during the consultation which in the best case are non-hazardous and which in the worst case are classified for Aquatic Acute 1, Aquatic Chronic 1, Skin. Irrit. 2, Eye Irrit. 2, Acute Tox. 4 and STOT SE 3. As such, transition from strontium chromate – which is a non-threshold carcinogen – to one of these substances would constitute a shift to less hazardous substances.

7.1.6.6 Conclusion on suitability and availability for molybdate-based corrosion inhibitors

Available information for molybdate-based primers showed that the corrosion performance on aluminium alloys and chemical resistance are clearly insufficient. Current formulations failed to meet the minimum requirements of the aerospace industry already at laboratory scale. During the consultation, R&D at very early laboratory scale was reported.

In summary, molybdate-based primer/paint systems are technically not equivalent to strontium chromate-based products for use as bonding or basic primer and are therefore not a general alternative. It is questionable if these systems will qualify for further R&D efforts within the aerospace sector, since other substances seem to be more promising.

7.1.7 Rare earth-based corrosion inhibitors (cerium (Ce), praseodymium (Pr))

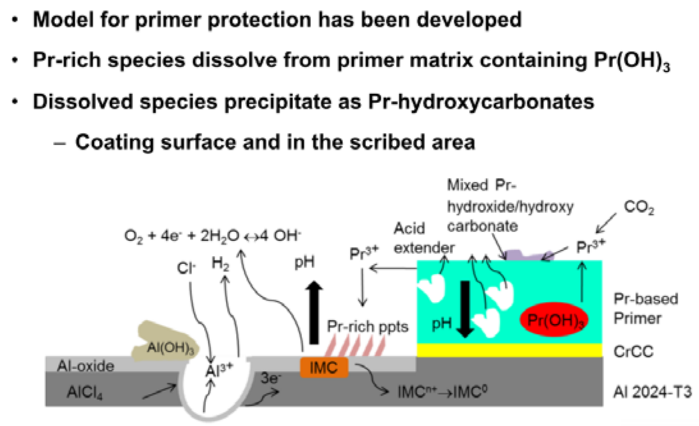
7.1.7.1 Substance ID and properties

In 1980, it was first demonstrated that Rare-Earth (RE)-based compounds can be used as corrosion inhibitors in an aqueous environment. Primers containing RE compounds had been shown to provide protection to Al alloys but the mechanism of protection had not been investigated. Based on previous studies, RE compounds are not inherently protective. Instead, protection requires that the proper phase be present in the right type of coating. Selected RE-based compounds are currently being used to replace chromates in certain military applications (Fahrenholtz, 2012).

General information on properties of relevant RE-based corrosion inhibiting agents as well as the overall risk for human health and environment is provided within Appendix 3.1.7.

7.1.7.2 Technical feasibility

General assessment: Previous laboratory research showed that Pr compounds in combination with other additives are effective corrosion inhibitors in epoxy polyamide primers. These primers are commercially available and have been qualified to DoD requirements. The Pr-based inhibitors are effective in epoxy-polyamide primer systems when the primer is deposited onto high strength aluminium alloys with chromate loaded conversion coating. The primers do not perform as well when they are applied on non-chromate conversion coatings or bare Al alloys. The phase of the Pr compound and the solubility of other additives affect corrosion protection, but corrosion protection mechanisms have not been fully investigated. It is postulated that dissolution of Pr-rich species from the coating during exposure to corrosive environment is the key driver for the protection mechanism (Fahrenholtz, 2012).



- **Model for primer protection has been developed**
- **Pr-rich species dissolve from primer matrix containing $Pr(OH)_3$**
- **Dissolved species precipitate as Pr-hydroxycarbonates**
  - **Coating surface and in the scribed area**

Figure 23: Mode of action for praseodymium-rich species (Fahrenholtz, 2012)

Corrosion resistance: First test series performed in the laboratory on scribed AA2024-T3 panels showed that primer systems based on Pr_2O_3 or Pr_6O_{11} did provide corrosion protection for up to 3000 h in ASTM B117 when applied after chromate conversion coating, but clearly not after Cr(VI)-free conversion coatings. Even if the corrosion performance of a Cr(VI)-free primer may meet some of the general specification of civil aviation, Cr(VI)-free primers which are intended for use in aerospace applications would have to meet extended requirements to ensure that a Cr(VI)-free technology exhibits the same corrosion protection and adhesion performance as currently used Cr(VI)-based products. Furthermore, it must be stated that the primer was only tested in one system. No further information on other standard and extended corrosion tests, such as FFT and AIE were provided.

Ce salts are under investigation as additives in different primer/paint systems. In combination with several epoxy-based phosphate containing coating systems, the extended corrosion requirements of the aerospace industry were not met. After 3000 h on substrates pre-treated with CCC and on TSA creepage from scratch was > 1.25 mm and around 1.5 mm, respectively. Pitting appeared around 3000 h. Results from filiform corrosion test (EN 3665) confirmed that minimum requirements for filiform corrosion were achieved. Some companies require extended corrosion protection up to 3000 h. If companies require increased performance in tests according to EN 3665, ISO 9227 and/or ISO 7253, the tested corrosion inhibitors do not constitute suitable alternatives.

Addition of small amounts of cerium oxide (0.5% by weight) to a Mg-rich primer was shown to significantly improve the protection performance of a Mg-rich primer on AZ91D magnesium alloy, by increasing the corrosion potential and decreasing the current density of the alloy, which is beneficial for cathodic protection of the Mg particles (Wang et al, 2012).

In conclusion, the tested RE-based systems are currently part of research in several institutes and military surroundings but are far from being technically equivalent to Cr(VI)-based basic or bonding primer in aerospace applications. Even where only excellent adhesion promotion would be necessary, these systems failed to meet the specifications from the aerospace sector.

Summary and overview of the conclusion regarding feasibility of epoxy/PU-based primer containing RE-compounds as corrosion inhibitors	
Corrosion resistance	Adhesion
🟥	🟥

7.1.7.3 Economic feasibility

Against the background of significant technical failure of these alternate systems, no detailed analysis of economic feasibility was conducted. However, chemical cost can be higher compared to Cr(VI)-compounds.

7.1.7.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances and products reported during the consultation were reviewed for comparison of the hazard profile. In addition, publically available information on specific alternative products was evaluated. Based on the available information on the substances used within this alternative (see Appendix 3.1.7), they are in worst case classified as Aquatic Acute 1, Aquatic Chronic 1, Skin Irrit. 2, Eye Irrit. 2, STOT SE 3. As such, transition from strontium chromate – which is a non-threshold carcinogen – to one of the above mentioned alternative inhibitors/products would constitute a shift to less hazardous substances.

7.1.7.5 Availability

According to literature research, commercial products based on praseodymium are already in use in the military sector, while no experience exists for their use in civil aviation. As stated above, the military standards such as MIL-DTL-53022 are not comparable to the requirements of the civil aviation industry.

During the consultation, it was reported that very few R&D with RE-based compounds is ongoing at paint manufactures at early laboratory scale. To date, REs are tested mostly as additives in primer formulations. If successful identification of an inhibitor occurred in the laboratory, the additional time required for product validation at laboratory scale is >1 year, provided all required tests are passed successfully. Thereafter, the formulation would be proposed for testing at OEM, where 3-5 years might be necessary until the substance could enter qualification phase (refer to chapter 5.1). Altogether, in a best case scenario, for passing all TRL stages until deployment of newly developed compounds at least 15 years after a viable candidate is developed are necessary, if no major drawbacks occur.

In summary, the relevance of RE-based formulations alone or in combination with other substances as inhibiting agent in primer/paint formulations is questionable.

7.1.7.6 Conclusion on suitability and availability of RE-based corrosion inhibitors

Few development products containing RE-compounds as standalone or in combination with other inhibiting have been reported. They failed to meet the minimum corrosion and adhesion requirements of the aerospace industry already at laboratory scale. During the consultation, few R&D at very early laboratory scale was reported.

In summary, RE-based primer/paint systems are technically not equivalent to strontium chromate-based products for the use as bonding or basic primer and are therefore not a general alternative. It is questionable if these systems will qualify for further R&D efforts within the aerospace sector, since other substances seem to be more promising.

7.1.8 Zinc-based corrosion inhibitors

7.1.8.1 Substance ID and properties

Coatings containing zinc are mainly used for the long-term corrosion protection of industrial and marine steel constructions (such as steel infrastructure, pipelines, bridges, windmills, and offshore drilling platforms) and the temporary protection of steel sheets (shop primers) during new building of ships (Verbiest, 2013).

A distinction between “zinc-rich” primers and “zinc” primers can be made. Zinc dust is the corrosion inhibiting agent in zinc-rich primers, and is present in concentrations > 80 % (w/w) in dry paint films, providing cathodic protection to steel. Zinc primers usually have zinc concentrations in the range of 25-70 % (w/w) and are used to provide only temporary corrosion protection. Various zinc-containing primers are available on the market. Typical applications for inorganic zinc silicates include the use on barge decks (due to very good abrasion resistance), pipelines, power plants, power transmission lines, bridges, ships, tankers (interior and exterior surfaces, including storage tanks, oil rigs, and offshore drilling platforms), water tanks, and steel to be primed in the shop. Organic zinc epoxies are usually applied as high-performance coatings with good flexibility to steel substrates (poorly pre-treated steel; maintenance projects; touch-up of zinc silicate shop-primed steel). General information on properties of relevant zinc-based anticorrosion systems and the overall risk for human health and environment is provided within Appendix 3.1.8.

7.1.8.2 Technical feasibility

Corrosion resistance: Zinc rich primers (> 80% zinc in dry paint) provide good galvanic corrosion protection on steel substrates, and are used in industrial and marine constructions. For development products, salt spray test according to ASTM B117 revealed no corrosion after 1000 h exposure of scratched steel panels. However, zinc-based primers fail in the protection of Al 2024-T3. Formulators tested various zinc inhibitors in amine or epoxy matrices as standalone and in combination with phosphate and cerium salts. The corrosion requirements within the aerospace sector (>3000 h in ISO 9227 and up to 6000 h in ISO 7253) are clearly not met. While results from filiform corrosion test (EN 3665, 960 h) with epoxy primer containing zinc pigments satisfied criteria for substrates pre-treated with chromate-free conversion coating and on TSA. Testing according to ISO 9227 and ISO 7253 was insufficient: after 1000 h creepage from the scratch was > 2 mm.

When zinc-based formulations were tested on clad and unclad aluminium alloys, performance in the salt spray test (3000h, <1.25 mm), and the alternating immersion-emersion test (1500 h; 1.25 mm) was acceptable, but corrosion from scratch exceeded the acceptable maximum of 2 mm in the filiform corrosion test (960 h, >3 mm). Moreover, all tested zinc-based formulations failed the crevice corrosion test. Furthermore, zinc pigments do not provide active corrosion inhibition. Thus, long-term corrosion protection on scratched surfaces is deemed to be insufficient.

Adhesion: Adhesion performance of zinc-based inhibitors in coatings on aluminium alloys and in epoxy primer on AA2024-T3 pre-treated with TSA is sufficient.

Chemical resistance: In addition, sufficient performance of zinc-based inhibitors tested in coatings on aluminium alloys with regard to chemical resistance was demonstrated in water, hydraulic fluid, fuel and humidity. The evaluated zinc-based inhibitors in epoxy coatings also passed tests for chemical resistance on AA2024-T3 pre-treated with TSA in water and hydraulic fluid.

Other parameters: The zinc-based inhibitors tested in coatings on clad and unclad aluminium alloys fulfilled the requirement regarding layer thickness, hardness, impact resistance, and flexibility.

According to information from this industry sector, R&D for these substances is on hold.

In addition to information provided during the consultation, publically available performance results of zinc containing inhibitors are presented here. In general, these products were tested on steel plates, so their corrosion performance cannot be easily transferred to high strength Al alloys which are used in aerospace, marine, automotive and other applications. On steel plates, the results from the salt spray tests according to ASTM B 117 and ISO 9227 with orthophosphate-based systems modified with zinc indicate an inferior protection of the substrate, with corrosion appearing after 550-860 h. On bare aluminium, the organically modified zinc orthophosphate hydrate in epoxy matrix showed significantly better performance than zinc phosphate after 2218 h, while in general corrosion was visible for all samples tested. Further testing results on different parameters and different substrates like Al alloys are not available for these products.

Summary and overview of the conclusion regarding feasibility of epoxy/PU-based primer containing zinc compounds as corrosion inhibitors				
Corrosion resistance	Adhesion	Layer thickness	Chemical resistance	Compatibility with substrate
🟥	🟩	🟩	🟩	🟩

7.1.8.3 Economic feasibility

Against the background of significant technical failure of these alternate systems, no detailed analysis of economic feasibility was conducted. However, based on the literature research and consultations there is no indication that the discussed alternative is not economically feasible.

7.1.8.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances and products reported during the consultation were reviewed for comparison of the hazard profile. Zinc compounds that have been tested in paint/primer are in the best case not classified. In the worst case, they have classifications as Pyr. Sol. 1, Water-react. 1, Aquatic Acute 1, Aquatic Chronic 1. As such a transition from strontium chromate - a non-threshold carcinogen - to zinc-based inhibitors would constitute a shift to less hazardous substances.

7.1.8.5 Availability

Zinc-containing primer formulations are available on the market. Few information on their performance is publically available for steel substrates and bare aluminium.

During the consultation, it was stated by the aerospace sector that R&D efforts are currently on hold. Few paint manufacturers reported that zinc-based primer/paint systems are currently in the very early laboratory phase. Thus, the final success of zinc-based alternatives cannot be determined at present. If successful identification of an inhibitor at laboratory scale occurs, the additional time required for product validation on laboratory scale is >1 year, provided all required tests are passed successfully. Thereafter, the formulation would be proposed for testing at OEM, where 3-5 years may be necessary until the substance could enter qualification phase (refer to chapter 5.1). Altogether, in a best case scenario, for passing all TRL stages until deployment of newly developed compounds at least 15 years after a viable candidate is developed are necessary, if no major drawbacks occur.

In summary, the relevance of zinc-based formulations alone or in combination with other substances as inhibiting agent in primer/paint formulations is questionable.

7.1.8.6 Conclusion on suitability and availability for zinc-based corrosion inhibitors

Several development products containing zinc compounds as standalone or in combination with other inhibitors have been tested on Al alloys and on steel. All of them failed to meet the minimum corrosion requirements of the aerospace industry already at laboratory scale. Several zinc-based inhibitors are available on the market. Their performance with regard to corrosion is not sufficient to comply with the overall minimum requirements of the aerospace sector, especially with regard to extended corrosion. During the consultation, few R&D at very early laboratory scale were reported.

In summary, zinc-based primer/paint systems are technically not equivalent to strontium chromate-based products for use as bonding or basic primers and are therefore not a general alternative. It is questionable if these systems will qualify for further R&D efforts within the aerospace sector, since other substances seem to be more promising.

7.2 Electrocoat primer technology

7.2.1 Substance ID and properties

The composition and properties of the Cr(VI)-free electrocoat primer are proprietary. Investigations are underway to develop a paint specifically designed for the alloys commonly used in the aerospace industry (Collinet M., Labouche D. 2012). In comparison to standard primers which are usually sprayed onto metal parts, in the electrocoating, or electrodeposition process, after pre-treatment metal parts are dipped into an electrically charged tank of primer. Electrical current is used to apply the coating to a conductive substrate via anodic or cathodic deposition (see **Figure 24**).

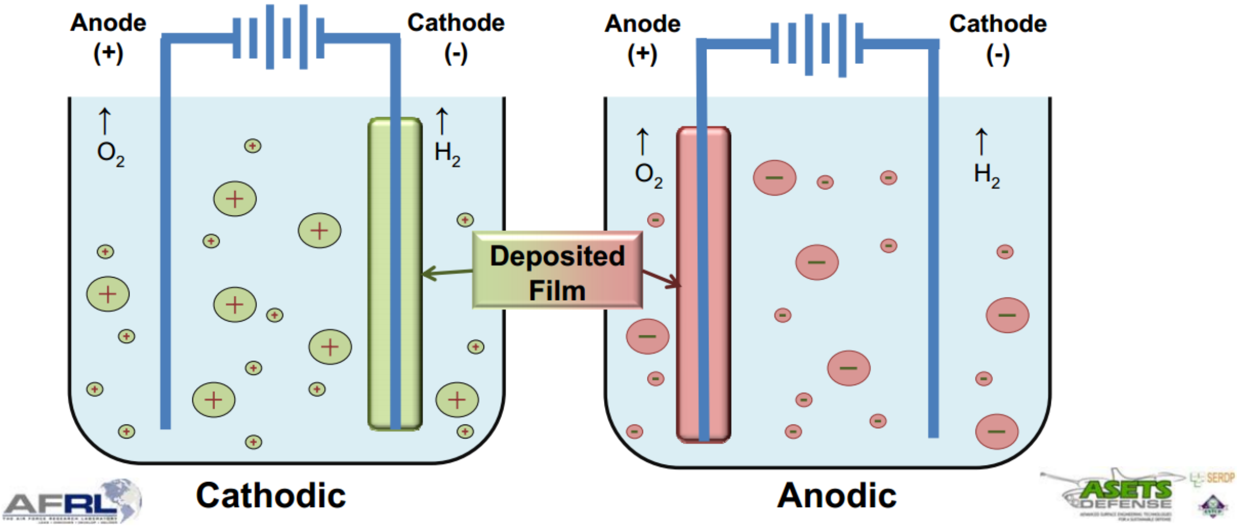


Figure 24: Electrodeposition process, cathodic and anodic deposition (from Pawlik, 2009)

Within the military sector, the cathodic electrocoat deposition process is applicable for the deposition of positively or negatively charged paint particles (depending on the substrate and application).

After coating, the metal part is moved to the rinse stage. In the final step the coated metal parts are thermally cured (30 minutes at 93 °C) to achieve the final coating properties. Curing parameters (time and temperature) can vary according to the substrate, the coated surface, the part thickness and other parameters. According to the supplier "*the electrocoat process can be fully automated and offers increased material utilisation*". A schematic overview of the components of an electrocoat conveyor process can be found in **Figure 25**. After thermal cure parts can be immediately handled.

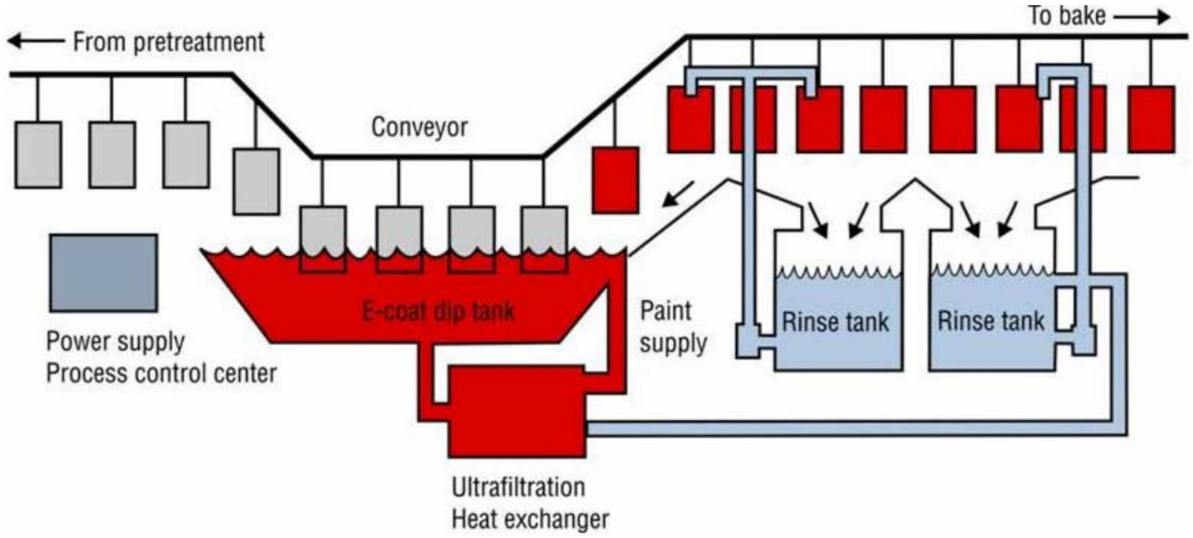


Figure 25: Components of an electrocoat conveyor process (Pawlik, 2009)

The substance identity and composition of the electrocoating formulation used in the process is not known as this is proprietary of the supplier and only limited information on the risk to human health and environment from this alternative is provided in Appendix 3.2.

7.2.2 Technical feasibility

A first Cr(VI)-free electrocoat-application primer has been developed for the global airframe manufacturers and subcontractors to coat parts for commercial, military and general-aviation aircraft.

General assessment: This alternative treatment is investigated to replace the combination "chemical conversion + primer" (when it is applied with a thickness of 12 to 20 µm) and could also be a replacement for anodizing (when it is applied with a thickness of 5 µm) or the combination "anodizing + primer" (when it is applied with a thickness of 17-30 µm). The performance results which are reported in the following paragraphs are determined within the framework of testing for the military sector. In this sector, some Cr(VI)-free coatings must fulfil specific military standards such as MIL-PRF-85582 class N which are not comparable to the requirements of the civil aviation industry. Therefore, coatings developed for military purposes are not directly applicable for the general structure for civil aircraft, as the frequency of military planes is very low compared to civil planes running on a daily basis, as well as considerations related to the systems and performance envelope of military aircraft. Based on these daily demands to ensure the airworthiness of civil aircraft, the requirements are much more comprehensive.

Data from literature assumed that key performance criteria were met for military applications (corrosion, adhesion, flexibility, chemical resistance against different fluids) on Al alloys 2024 and 7075 (Pawlik, 2009). Results of beach exposure testing on corrosion performance are still ongoing (Lingenfelter, 2012). Data on corrosion performance is currently inconsistent.

Corrosion resistance: Tests according to ASTM B117 and EN3665 revealed an insufficient corrosion performance on Al alloys with length from scratch exceeding 3 mm after 3000 h and 720 h, respectively. In contrast, another research program reported average length of blisters at the scratch is 1 mm on clad 2024-T3 and 0.25 mm on bare 2024-T3 (Collinet et al, 2012) after 3000 h-exposure in the filiform corrosion test (EN 3665) and the neutral salt spray test (ISO 9227). After 6000 h in the neutral salt spray test, results still meet the standard civil aviation requirements. The system does not provide active corrosion inhibition and is as such no replacement for parts that need corrosion protection including active corrosion inhibition.

However, when the aerospace industry shared their experience on this new application, their test results are not consistent with the current research programs. First results from the aerospace/helicopters sector (civil and military) for corrosion resistance after beach exposure (atmospheric corrosion) and accelerated aging have shown lower performances than reference (chemical conversion coating + Cr(VI) primer).

Adhesion properties: While in general, few issues on adhesion were reported, it has also been noted that electrocoats showed insufficient adherence with various sealants used. Here, adhesion enhancer would be needed. Further tests are needed to improve the performance on this requirement.

Other parameter: It was also indicated that higher performances of the electrocoat systems in terms of bending, scratch resistance and corrosion resistance after salt spray exposure compared to reference systems were achieved. It is reported that the electrocoat primer is also applicable for complex-shaped parts and can be coated uniformly.

In contrast to the information above, this process is not suitable for assembled aircraft. A major drawback of this treatment is that it is a dip coating process, it can only be applied to OEM and MRO parts that can be removed from the aircraft during overhaul. Difficulties were also observed with electrocoat stripping, as it has to be carefully evaluated which products are suitable for this process. Indeed, this technology requires development of a new repair and touch-up process Therefore, another limitation of this process is that electrocoated parts can currently only be **repaired** by using conventional Cr(VI)-containing anti-corrosive primers. In conclusion it was confirmed that with this alternative, the current aerospace standards cannot be completely met (especially for conductive requirement, and touch-up & repair process). The produced layers are not conductive and as stated above repairing processes have to be redefined.

Summary and overview of the conclusion regarding feasibility of electrocoat primer technology					
Corrosion resistance (long term)	Active corrosion inhibition	Complex geometries	Adhesion	Chemical resistance	MRO applications
🟥	🟥	🟩	🟩	🟩	🟥

7.2.3 Economic feasibility

Against the background of significant technical failure of these alternate system, no detailed analysis of economic feasibility was conducted. Life cycle costs have not been established. There is an initial capital requirement for the baths. However, based on the literature research and consultations there is no indication that the discussed alternative is not economically feasible.

7.2.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information reported during the consultation were reviewed for comparison of the hazard profile. Substance identity and composition of the resins system, pigment paste and anticorrosion paste used in the electrocoating process is not known as this is proprietary of the supplier. Based on the information reported by the supplier during the consultation (see Appendix 3.2), substances used within this alternative are classified as Eye Irrit. 2, and Aquatic Chronic 3 as well as Skin Irrit. 2, respectively. As such, transition from strontium chromate – which is a non-threshold carcinogen – to this process would constitute a shift to less hazardous substances.

7.2.5 Availability

The electrocoat primer technology was originally developed for the automotive industry and is currently being adapted to fulfil requirements from other sectors. An electrocoat primer was commercially launched in 2012 and is qualified to SAE International’s Aerospace Material Specification (AMS) 3144 for anodic electrodeposition primer for aircraft applications (publically available information as of January 2014). SAE International is a global association of technical experts in the aerospace and automotive industries. Their documents serve as recommendations for the transportation sector mainly within the US and Canada but do not carry any legal force. Within the aerospace industry in the EU, R&D efforts have been ongoing for many years, however so far these systems have not passed the early development phase.

7.2.6 Conclusion on suitability and availability for electrocoat primer technology

A Cr(VI)-free electrocoat primer is available on the market and currently qualified according to AMS 3144. While the overall performance may be sufficient for the military sector, this primer system is not yet generally qualified for civil aviation. The daily demands particularly with regard to corrosion performance, are much more comprehensive to ensure the airworthiness of civil aircraft. This process is not applicable for assemblies and assembled aircraft. Further technical limitations were highlighted during the consultation phase.

In summary, electrocoat primer system shows some important technical limitations which clearly do not qualify them to be a general alternative to Cr(VI)-based primer/paint systems so far. Since these systems are in early research stages (no TRL defined yet), for substitution of strontium chromate in basic or bonding primer applications at least 15 years after a viable candidate is developed is anticipated until implementation of the alternative products into the supply chain.

7.3 Silane-based processes including sol-gel coatings

7.3.1 Substance ID and properties

Silane is an inorganic compound with the chemical formula SiH_4. It is the chemical source molecule for silanes, which are a chemical group of saturated hydrosilicons with the general formula Si_nH_{2n+2}. Silanes can be linear or branched. Organofunctional silanes are based on silicon and contain organic and inorganic groups in a single molecule. The general structure is $(XO)_3Si(CH_2)_nY$, with OX = hydrolyzable alkoxy group, Y = organofunctional group (e.g. amine, epoxy or isocyanate …). As two different types of reactive groups are present in the molecules, silanes are able to provide chemical bonding between organic and inorganic materials. Thus, they are commonly used as adhesion promoters or coupling agents. Siloxanes are a functional group of chemicals characterised by the Si–O–Si linkage. Chemical source molecules include oligomeric ($H(OSiH_2)_nOH$) and polymeric hybrids ($(OSiH_2)_n$). Branched siloxanes also exist; each silicium center is separated by one oxygen atom.

Sol–gel protective coatings have shown excellent chemical stability, oxidation control and enhanced corrosion resistance for metal substrates (Wang & Bierwagen, 2009). Today, sol gel technology is rapidly expanding, and extensive R&D effort is being made. Many new products are appearing on the market, especially since the advent of hybrid and nanocomposite materials. This method is used for the fabrication of metal oxides, in particular for oxides of silicium, zirconium and titanium. In general, monomers that are contained in a colloidal solution ("sol") serve as precursors for generation of an integrated network or "gel" (discrete particle or network of polymers). The process involves evaporation of the solvent and the subsequent destabilisation of the sols leads to a gelation process and the formation of a transparent film due to the small particle size in the sols. Depending on the substrate size and shape, different technologies can be applied.

Apart from silica, a number of other substances can be used in the sol-gel process, e.g. aluminium-2-propylate, aluminium-2-butylate, zirconium propylate, titanium, titanium ethylate, and titanium-2-propylate.

General information on properties and hazard classification and labelling of substances used in Sol gel process are given within Appendix 3.3.

7.3.2 Technical feasibility

General assessment – Superprimer: Silane-based systems for corrosion protection have been studied at the University of Cincinnati since the early 1990s. Silane films were modified by adding inhibitors, nanoparticles or colorants to enhance the properties such as corrosion protection. In the next stage – which was entered in 2004 – silanes and organic resins were combined to achieve properties of both, effectively bonding to the substrate and achieving considerable film build up to 20 µm. These hybrid organic-inorganic coatings are named as "superprimers". As the superprimer contains more silanes than required for crosslinking of the polymer, the silanes form a siloxane network. Silanol groups contained herein react with the metal hydroxide. The intention behind the development of these superprimers is to replace the combination "chemical conversion + primer", e.g. on aerospace aluminium alloys. In addition to insufficient corrosion resistance, the current major drawbacks relate to the mechanical properties and chemical resistance. To date, these formulations are at very early laboratory research scale and are some way from being applied on aircraft.

General assessment – Sol-gel: A more promising application is the Sol-Gel process. The first Sol-Gel applications are used as an alternative conversion coating for painting and bolding applications or on the exterior fuselage of aluminium parts with low corrosion risk, due to clad layer.

From literature research, it was highlighted that thin films without the need for machining or melting can be applied. Literature also highlights that complex shapes can be coated with the sol-gel coating process (Wang & Bierwagen, 2009):

According to literature, current challenges with this process include the following:

- Interface properties of sol-gel coatings (adhesion, delamination) determine the quality of the sol-gel coating. General approaches or methods to evaluate these properties have not yet been established.
- Processing times are very long as the curing process is performed at high temperatures
- Due to a substantial volume contraction and internal stress accumulation caused by the large amount of evaporation of solvents and water, cracks can easily form in the coating. Therefore,

> the formation conditions of the sol-gel coatings have to be carefully controlled during the drying process (Wang & Bierwagen, 2009).

These scientific statements and expectations from Wang and Bierwagen (2009) are in contrast to industry experience with sol-gel coatings.

Corrosion resistance: Sol-gel chemistries by themselves do not provide significant stand-alone corrosion resistance, therefore rely on additives or subsequent coatings to provide the corrosion resistance to meet part requirements. Currently there are no known additives to the silane matrix that have shown stand-alone corrosion resistance that meets aerospace requirements. First generation Sol-gel coatings (aiming at adhesion promotion) generally prevent corrosion by their function as a physical barrier, rather than through active corrosion protection. Furthermore, coatings like e.g. ZrO_2-based sol-gels do not provide active corrosion inhibition (Paussa, 2011), thus not providing corrosion protection of scratched surfaces. Therefore, sol-gel coatings require a suitable anti-corrosion coating on top.

Sol-gel coatings in combination with a Cr(VI)-free primer can be used as alternative for the use on steel and aluminium for the exterior of aircraft / helicopters where the corrosion inhibition requirements are less demanding compared to interior applications and applications on structural aircraft components. Especially the long-term corrosion requirements for structural components, salt spray and filiform corrosion tests are not met when sol-gel coatings are combined with Cr(VI)-free primers.

Adhesion: In addition, problems are reported by industry for sol-gel coatings on aluminium surfaces. The sol-gel coatings investigated as alternative for chromate conversion coatings within the aerospace sector are not directly in contact to the metal surface but they are in interaction to a very thin aluminium oxide film. Therefore, the performance of the sol-gel coating is strongly dependent on the properties of the pickling solution or the surface pre-treatment and conditions used prior to the sol-gel coating. As a consequence, adhesion and corrosion protection properties cannot only be determined by evaluation of the sol-gel system. Furthermore, flexibility and film thickness play also an important role and have to be adapted accordingly.

Layer thickness: Layer thickness of the sol-gel coating is a significant factor in the performance of the coating: thin layers may not provide sufficient corrosion protection, while embrittlement may occur in thick layers. Therefore, where the formulation is being used as a corrosion protection layer, achieving the required level of corrosion protection may require a thick sol-gel layer so that the coating becomes brittle, thereby compromising corrosion protection.

Reproducibility: All these considerations indicate that the process for the industrial application of sol-gel coatings is complex and has currently limited reproducibility

Other parameters: Several companies stated that sol-gel coatings improve the adhesion of a primer, and have also positive influence on chemical resistance and water resistance due to the improved adhesion properties.

The University of Toulouse in cooperation with industry is working on the SOL-GREEN project which is investigating and developing anti-corrosion sol-gel coatings for aluminium alloys used in aeronautical industry (Cerda et al, 2011). First results were published from this multi-company project. Tests with hybride coatings deposited on AA2024-T3 were reported to show a salt spray resistance > 500 h (test method not given) at layer thicknesses > 4 µm (tested layer thicknesses: 1.1 – 9.1 µm). The minimum corrosion requirements for aerospace applications as reported during the consultation are often much higher, especially with regard to long-term corrosion which can be >> 6000 h (ISO 9227).

It could be demonstrated that sol-gel coatings are efficient barriers. This barrier effect can be increased by the addition of cerium and boehmite nanoparticles to the coating, which provides active corrosion protection and inhibits the corrosion propagation into the substrate corrosion performance was improved up to 1400 h.

Cerium compounds, e.g. cerium nitrate have been demonstrated to “precipitate on the aluminium substrates following deposition mechanisms which are controlled by the chemical composition of the metal surfaces. The cerium precipitation occurs in a wide range of pHs limiting the corrosion activity of very reactive aluminium alloys like AA2024-T3.” (Paussa, 2011). In parallel, the process development of the SOL-GREEN project aims towards processing of industrial objects with **complex geometries** since satisfying results were only achieved on specimens, but not on whole parts. Layer thickness and heterogeneities of sol-gel coats applied via dip coating were investigated by means of test objects with complex geometries (representative body, see **Figure 26**).

Figure 26: Representative body used in the assessment of layer thickness and heterogeneity of sol-gel coats applied by means of dip coating (Cerda, 2011)

Dip coatings with standard sol-gel revealed areas of thickness heterogeneities from 5 to 30 µm. In order to overcome this issue the viscosity of the sol-gel solutions was decreased by means of dilution. Electrochemical Impedance Spectroscopy (EIS) measurements after 1 h in a 0.05M NaCl solution revealed maintenance of the barrier effects even after dilution of the sol. The dip-coating process of an industrial object with a diluted solution resulted in a decrease of thickness heterogeneities (range from 4 to 12 µm). However, additional R&D efforts are needed to further improve this approach and to finally upscale the system for industry applications.

Based on these finding and the mode of action, it can be summarised that sol-gel coatings are interesting systems which currently show various technical limitations. To date, it is not known if this is a general alternative for the applications within the here described use; the TRL is still low at present.

Summary and overview of the conclusion regarding feasibility of Sol-Gel systems				
Corrosion resistance	Adhesion	Layer thickness	Reproducibility	Complex geometries
🟥	🟨	🟥	🟥	🟥

7.3.3 Economic feasibility

Against the background of significant technical failure of these alternate systems, no detailed analysis of economic feasibility was conducted. However, based on the literature research and consultations there is no indication that the discussed alternative is not economic feasible.

7.3.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances reported during the consultation were reviewed for comparison of the hazard profile. In addition, publically available information on specific alternatives products was evaluated. Please note that the exact substance identity and composition of products used in the Sol-Gel process is very often not known as this is confidential business information of suppliers. Based on the available information on substances used within this alternative (see Appendix 3.3), the worst case is presented by Vinyl trimethoxysilane (VTMS), which is classified as Flam. Liq. 3, Acute Tox. 4, Eye Dam. 1, Skin Irrit. 2, Eye Irrit. 2, STOT SE 3, Asp. Tox 1, Muta. 1B, Carc. 1B. Additionally VTMS is included in the CoRAP (Community rolling action plan), indicating substances for evaluation by the EU Member States in the next three years. The evaluation aims to clarify concerns that the manufacture and/or use of these substances could pose a risk to human health or the environment. As such, even transition from strontium chromate – which is a non-threshold carcinogen – to the above mentioned alternative inhibitor/product, which represents the worst case scenario, would constitute a shift to a less hazardous substance. However, as some of the alternate substances used are as well under observation, the replacement has to be carefully evaluated on a case by case basis.

7.3.5 Availability

Several Sol-gel coatings have already reached the market and are approved by aerospace companies as a paint system, in applications where only good adhesion properties are needed (rather than for example, corrosion-prevention). Products based on aqueous solutions of zirconium salts, which are activated by an organo-silicon compound, are already approved by several companies within the aerospace sector. These products, based on organosiloxanes and zirconates provide good adhesion properties but are insufficient in terms of corrosion protection. Nevertheless, these systems are subject to comprehensive R&D efforts worldwide:

- the HITEA project covers many aspects of Cr(VI) replacement in the aerospace sector, also including a thorough analysis of Sol Gel Pre-treatment. In 2014, the tested alternatives are at TRL2. After the initial phase, the project will focus on a handful of promising alternatives, where further testing is conducted within the next years. Qualification (TRL6) will take up to 10 years from now. Sol-gel has been looked at previously as a pre-treatment and was considered not to be adequate as it gave good adhesion properties, but no anti-corrosion protection. It is currently being looked at again in the HITEA Project.
- the aim of the SOLCOAT project is to develop and improve a Sol Gel Coating for magnesium alloys for industrial manufacture and use. This project is on-going.
- In 2008, the multi-company project SOL GREEN was initiated for the development of protective coatings of Al/Mg alloys. Since these coatings solutions are not based on electrochemical conversion, but involve an alternative technology, the industrial production qualification is not expected before 2025. Phase 1 was not finished until 2013, showing that SOL GREEN 1 faces some technical issues. In addition to the main problem of insufficient corrosion performance, the layer thickness cannot be controlled adequately with the current dip coating processes: satisfying results were only achieved on specimens, but not on whole parts due to their complex geometries. Therefore, the main objective of SOL GREEN 2 is to

assess and develop an electrophoresis process to apply the anti-corrosion coatings through SOL-GEL technique for complex geometry parts. These challenges are currently ongoing and research is mainly conducted at laboratory scale (TRL 2) at university and in some partner’s plants. However, as mentioned above, this is a long term solution since for qualification and implementation of further applications at least 12-15 years will be needed.

7.3.6 Conclusion on suitability and availability for silane-based processes including sol-gel coatings

Commercial sol-gel coatings are currently available on the market which in theory can be used in combination with Cr(VI)-free top coats. These combinations, however, clearly do not provide sufficient corrosion protection with regard to the stringent requirements of the aerospace sector. Therefore, at present, several R&D projects are ongoing to find suitable anti-corrosion sol-gel coatings for use in the aerospace industry.

In summary, Cr(VI)-free sol-gel systems are technically not equivalent to Cr(VI)-based products and are therefore not a general alternative. Since these systems are in early research stages (TRL 2), for substitution of strontium chromate in basic or bonding primer applications at least 15 years after a viable candidate is developed is anticipated until implementation of the alternative products into the supply chain.

8. OVERALL CONCLUSIONS ON SUITABILITYAND AVAILABILITY OF POSSIBLE ALTERNATIVES FOR STRONTIUM CHROMATE

In the current document, potential alternatives to primer, and specialty coatings containing strontium chromate have been considered. Cr(VI)-based coatings are specified in the aerospace sector primarily because they provide superior corrosion resistance and excellent adhesion. These characteristics and the quality of the product are essential to the safe operation and reliability (airworthiness) of aircraft and spacecraft which operate under extreme environmental conditions. These structures are extremely complex in design, containing millions of highly specified parts, many of which cannot be easily inspected, repaired or removed.

Aircraft are one of the safest and securest means of transportation, despite having to perform in extreme environments for extended timeframes. This is the result of high regulatory standards and safety requirements. Assuming a technically feasible potential alternative is identified as a result of ongoing R&D, extensive effort is needed beyond that point before it can be considered an alternative to strontium chromate within the aerospace industry. This system robustly ensures new technology and manufacturing processes can be considered 'mission ready' through a series of well-defined steps only completed with the actual application of the technology in its final form (and under mission conditions). Referring to experience, it can take 20 to 25 years to identify and develop a new alternative, even assuming no drawbacks during the various stages of development of these alternatives. As a further consideration, while the implications of the development process in the aeronautic and aerospace sectors are clearly extremely demanding, specification of an alternative, once available, can be built into the detailed specification for new aircraft types (and new spacecraft). This is not the situation for existing aircraft types, for which aircraft may still be in production and/or operation. Production, maintenance and repair of these models must use the processes and substances already specified following the extensive approval process. Substitution of strontium chromate-based surface treatment for these 'legacy' craft introduces yet another substantial challenge; re-certification of all relevant processes and materials

In this context, the scale and intensity of industry- and company- wide investment in R&D activity to identify alternatives to Cr(VI) containing surface treatment systems is very relevant to the findings of the AoA. Serious efforts to find replacements for chromates have been ongoing within the aerospace industry for over 30 years. To date, Cr(VI)-free developmental products for primer replacement are at low maturity within the aerospace sector due to several technical failures as illustrated in **Table 9**. The current development status for alternatives is depicted in **Figure 27**.

Table 9: Overview of potential alternatives for corrosion-resistant coatings

Matrix/Process	Cr(VI)-free corrosion inhibitors	Application	Technical failure
Epoxy/PU-based primers with Cr(VI)-free inhibitors	Cr(VI)-free inhibitors (confidential)	BA, BO	• Corrosion resistance not sufficient
	Calcium-based corrosion inhibitors	BA, BO	• Corrosion resistance not sufficient • Adhesion not sufficient
	Organic corrosion inhibitors like 5-methyl-1H-benzotriazol	BA	• Corrosion resistance not sufficient • Chemical resistance not sufficient
	Phosphate-based corrosion inhibitors ‡	BA, BO	• Corrosion resistance not sufficient
	Magnesium-based corrosion inhibitors ‡	BA, SP	• Corrosion resistance not sufficient • Compatibility with various substrate not sufficient

Matrix/Process	Cr(VI)-free corrosion inhibitors	Application	Technical failure
	Molybdate-based corrosion inhibitors	BA, BO	• Corrosion resistance not sufficient • Adhesion not sufficient
	Rare earth-based corrosion inhibitors	BA, BO	• Corrosion resistance not sufficient • Adhesion not sufficient
	Zinc-based corrosion inhibitors	BA	• Corrosion resistance not sufficient • Adhesion not sufficient
Electrocoat primer technology	Various ‡	BA, SP	• Corrosion resistance (long-term) not sufficient • MRO applications
Silane-based processes including Sol-gel coatings	Sol-gel coatings ‡	BA, BO, SP	• Corrosion resistance not sufficient • Complex geometries
BA (Basic primer); BO (Bonding primer); SP (structural primer) ‡ only some substances in this group may be considered possible alternatives;			

Technical limitations are mainly determined as clearly insufficient corrosion performance, as one of the key requirement in the aerospace sector. Especially, no detailed information on long term performance of these systems which are intended for use in civil aircraft to ensure airworthiness and that a Cr(VI)-free technology exhibits the same corrosion protection and adhesion performance are currently available. The risk is the multiplicity of corrosion inhibition concepts not well assessed.

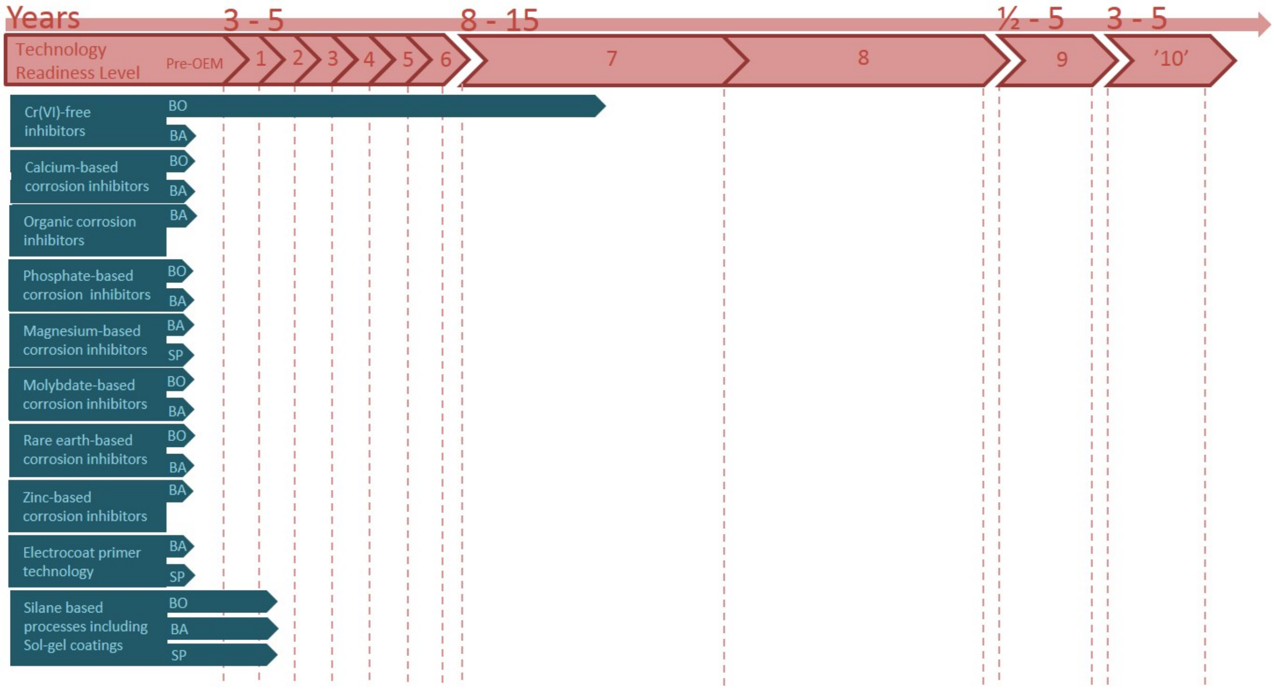


Figure 27: Development status of alternatives. BA (Basic primer); BO (Bonding primer); SP (structural primer).

It is important to note that the readiness levels indicated in **Figure 27** are best case scenarios for single OEMs/applications only and do not reflect the general development status of the aerospace sector.

For **basic primer and structural primer applications** several developmental products based on epoxy/PU-matrices are tested on Al alloys. Their overall performance is not sufficient to comply with the minimum requirements of the aerospace sector, especially with regard to extended corrosion protection. Further R&D in very early laboratory scale was reported, but none of the formulations reached TRL status yet. For passing all TRL stages until deployment of newly developed compounds at least 15 years after a viable candidate is developed are necessary, if no major drawbacks occur.

For **bonding primer applications**, first epoxy/PU-based products showed promising performance with regard to standard corrosion testing. R&D is far advanced for steel substrates, where first implementations may be expected within the next 5-7 years. For other substrates, with high copper containing Al alloys as most important ones within the aerospace sector, this process will take even longer. For a full implementation of bonding primer alternatives on all substrates plus for MRO applications, at least 15 years are necessary.

In summary, Cr(VI)-free primers, paints and specialty coatings currently do not represent a general alternative for the replacement of strontium chromate containing formulations as described within this dossier. Taking the technical readiness level and the long lasting approval process into account (see **Figure 27**), it can be stated that it will take at least until 2025-2030 to develop and deploy alternate products into the whole supply chain of the aerospace sector. Therefore, a review period of 12 years is desirable to include potential drawbacks and safety margins in the replacement process of strontium chromate. Still, this timeframe coincides with optimistic estimates by the aerospace industry of the schedule required to industrialise alternatives to strontium chromate. Since the sunset date for strontium Chromate is in January 2019, the period of time covered runs until 2031.

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APPENDIXES

APPENDIX 1 – JUSTIFICATIONS FOR CONFIDENTIALITY CLAIMS

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APPENDIX 2 – INITIAL LIST OF POTENTIAL ALTERNATIVES TO CR(VI)-CONTAINING SURFACE TREATMENTS.

ID	Alternative Substance/ Alternative Process	Category
1	LTAVD (Low Temperature Arc Vapor Deposition)	This process is related to functional chrome plating replacement and not relevant for primer applications
2	5-methyl-1H-benzotriazol	Summarised under organic corrosion inhibitors (**Category 2**)
3	Silicon-based primer	This alternative is related to applications within the automotive sector and currently not relevant for primer applications within the aerospace industry
4	Acidic anodising – Nitric, boric, boric-sulfuric (BSAA), oxalic, tartaric, phosphoric, sulfuric acid anodising	This process is related to CAA replacement and as such not relevant for primer applications
5	Aluminium electrolysis	This process is related to CAA replacement and as such not relevant for primer applications
6	Case hardening: Carburising, CarboNitriding, Cyaniding, Nitriding, Boronising	This process is related to functional chrome plating replacement and not relevant for primer applications
7	Chromium-free electroplating (Cooper plating,Nickel-free electroplates and composites,Non-electrolytic zinc plating)	This process is related to functional chrome plating replacement and not relevant for primer applications
8	CVD (Chemical vapor deposition)	This process is related to functional chrome plating replacement and not relevant for primer applications
9	Detonation gun thermal spray process (D-Gun)	This process is related to functional chrome plating replacement and not relevant for primer applications
11	Epoxy-based primer systems containing Cr(VI)-free inhibitors	**Category 1**
13	Faraday Technologies' Faradaic process (Cr(III))	This process is related to functional chrome plating replacement and not relevant for primer applications
14	HVOF (High Velocity Oxy-fuel)	This process is related to functional chrome plating replacement and not relevant for primer applications
15	Iridite NCP (Al, F, Oxygen)	This alternative is related to chemical conversion coatings and not applicable for primer applications
16	Keronite (plasma electrolytic oxidation)	This alternative is related to chemical conversion coatings and not applicable for primer applications
17	Laser alloying and laser cladding	This process is related to functional chrome plating replacement and not relevant for primer applications
18	Mineral Tie-Coat (cathodic mineralisation)	This process is related to functional chrome plating replacement and not relevant for primer applications
19	Molybdates and Molybdenum-based processes	**Category 2**
20	Nanocrystalline coating (process: HVOF, Thermal spray processes)	This process is related to functional chrome plating replacement and not relevant for primer applications
21	Nickel/Tungsten/Boron electroplating	This process is related to functional chrome plating replacement and not relevant for primer applications
22	Organic corrosion inhibitors e.g. amines, N-Methyl-2-Pyrrolidone, diazocomponents, triazoles etc.	**Category 2**
23	Permanganate-based treatments	This alternative is related to chemical conversion coatings and not applicable for primer applications
24	Phosphate-based corrosion inhibiting agents	**Category 1**

ID	Alternative Substance/ Alternative Process	Category
25	Plasma diffusion	This process is related to functional chrome plating replacement and not relevant for primer applications
26	Plasma spraying	This process is related to functional chrome plating replacement and not relevant for primer applications
27	Polysulfide-based primer systems containing Cr(VI)-free inhibitors	This matrix-system is and not relevant for primer applications within this use
28	PU-based primer systems containing Cr(VI)-free inhibitors	Summarised in epoxy/PU-based primer systems containing Cr(VI)-free inhibitors (**Category 1)**
29	Sherardising - Non-electrolytic zinc-iron alloy coating	This process is related to functional chrome plating replacement and not relevant for primer applications
30	Silane/Siloxane	Compounds of Sol-Gel coatings, as such summarised there **(Category 1)**
31	Sol-gel coatings (e.g. Zr/Si oxide-based)	**Category 1**
32	Stainless steel	This material is not a general replacement, mass of material points against a replacement in majority of airframe components
33	Tagnite (inorganic Silica or vanadate)	This process is related to functional chrome plating/CCC replacement and not relevant for primer applications
34	TCP (Trivalent chromium plating)	This process is related to functional chrome plating replacement and not relevant for primer applications
35	PVD (Physical vapor deposition), Sputtering	This process is related to functional chrome plating replacement and not relevant for primer applications
36	Weld facing, Micro-arc welding: Electro Spark Deposition (ESD), Electro Spark Alloying (ESA)	This process is related to functional chrome plating replacement and not relevant for primer applications
37	Zinc-based materials (Zinc, Zinc-Tin, Zinc-aluminium, Zinc-Nickel-based passivation)	**Category 2**
38	Organometallics (Organic Zirconates, titanates)	This alternatives was not further assessed by the industry due to clearly insufficient performance
39	Aluminium phosphate-based corrosion inhibiting agent	Summarised under phosphate-based corrosion inhibiting agents **(Category 1)**
40	Zr or Ti fluoride (+ additives)	This alternatives was not further assessed by the industry due to clearly insufficient performance
41	Vanlube (Barium petroleum sulphonate)	This alternatives was not further assessed by the industry due to clearly insufficient performance
42	Oxide mixture of Zn,Ce,SR,W and Mo (Ecotuff)	This alternative is related to applications within the architectural sector and not relevant for primer applications within the aerospace industry
43	Tall oil fatty acid salt	This alternatives was not further assessed by the industry due to clearly insufficient performance
44	Alkylammoniumsalz of (2-benzothiazolylthio)succinic acid	This alternatives was not further assessed by the industry due to clearly insufficient performance
45	Ammoniumbenzoate	Summarised under organic corrosion inhibitors **(Category 1)**
46	Bariumsulfate	This alternatives was not further assessed by the industry due to clearly insufficient performance
47	Calcium compounds (Calcium-Borosilikate, Calciumcarbonate, Calciumhydroxide, Calciummetasilikate)	**Category 1**

ID	**Alternative Substance/ Alternative Process**	**Category**
48	Dinonylnaphthalindisulfonsäure	This alternatives was not further assessed by the industry due to clearly insufficient performance
49	Potassium salt	This alternatives was not further assessed by the industry due to clearly insufficient performance
50	Magnesium compounds (Mg Ferrite, Mg oxyaminophosphate)	**Category 1**
51	Manganacetat Dihydrat	This alternatives was not further assessed by the industry due to clearly insufficient performance
52	Sodium compounds (Natriumcarbonat, Natriummetasilikat, Natriumnitrit)	This alternatives was not further assessed by the industry due to clearly insufficient performance
53	Titanate	This alternatives was not further assessed by the industry due to clearly insufficient performance
54	Phosphor compounds (Phosphoroxide, phosphoric ester)	This alternatives was not further assessed by the industry due to clearly insufficient performance
55	Polycarboxylat	This alternatives was not further assessed by the industry due to clearly insufficient performance
56	RE-based applications (Rare Earth, e.g. cerium)	**Category 2**
57	Electrocoat primer technology	**Category 1**

APPENDIX 3 – INFORMATION ON RELEVANT SUBSTANCES FOR IDENTIFIED ALTERNATIVES

Appendix 3.1: Epoxy/PU-based primers with Cr(VI)-free inhibitors

Table 1: Substance IDs and properties for relevant substances

Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	4-methyl-m-phenylene diisocyanate	Physical state at 20°C and 101.3 kPa	Solid
EC number	209-544-5	Melting point	21°C
CAS number	584-84-9	Density	1.21g /cm^3 (25°C)
IUPAC name	2,4-diisocyanato-1-methylbenzene	Vapour pressure	0.015 hPa (20°C)
Molecular formula	$C_9H_6N_2O_2$	Water solubility	0.1-100 mg/L (reacts rapidly with water)
Molecular weight	174.15 g/mol	Flammability Flash point	Not highly flammable -
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Butane-1,4-diol	Physical state at 20°C and 101.3 kPa	Liquid (viscous, colourless)
EC number	203-786-5	Melting point	20°C (101.3 kPa)
CAS number	110-63-4	Density	1.02 g/cm^3
IUPAC name	Butane-1,4-diol	Vapour pressure	< 0.1 hPa (20°C)
Molecular formula	$C_4H_{10}O_2$	Water solubility	Miscible with water
Molecular weight	90.1 g/mol	Flammability Flash point	n/a -

Table 2: Hazard classification and labelling

Substance Name	**Hazard Class and Category Code(s)**	**Hazard Statement Code(s) (labelling)**	**No. of Notifiers (CLP inventory)**	**Additional classification and labelling comments**	**Regulatory and CLP status**
4-methyl-m-phenylene diisocyanate (CAS 584-84-9) (EC 209-544-5)	Skin irrit. 2	H315 (causes skin irritation)	n/a	Resp. Sens. 1; H334: C ≥ 0,1%	Harmonised classification-Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation)
	Skin sens. 1	H317 (may cause an allergic skin reaction)			
	Eye irrit. 2	H319 (causes serious eye irritation)			
	Acute Tox. 2	H330 (fatal if inhaled)			

Substance Name	**Hazard Class and Category Code(s)**	**Hazard Statement Code(s) (labelling)**	**No. of Notifiers (CLP inventory)**	**Additional classification and labelling comments**	**Regulatory and CLP status**
	Resp. Sens.1	H334 (may cause allergy or asthma symptoms or breathing difficulties if inhaled)			
	STOT SE 3	H335 (may cause respiratory irritation)			
	Carc. 2	H351 (suspected of causing cancer)			
	Aquatic chronic 3	H412 (harmful to aquatic life with long lasting effects)			
Butane-1,4-diol (EC 203-786-5) (CAS 110-63-4)	Acute Tox. 4	H302 (harmfull if swallowed)	599		
	STOT SE 3	H336 (may cause drowsiness or dizziness)			
	Acute. Tox 4	H302 (harmfull if swallowed)	117		
	Acute. Tox 4	H302 (harmfull if swallowed)			
	Eye Irrit. 2	H319 (causes serious eye irritation)	80		

APPENDIX 3.1.1: Cr(VI)-free inhibitors (confidential)

The substance identity and composition of the tested formulations is not known as this is confidential business information.

APPENDIX 3.1.2: Calcium-based corrosion inhibitors

Table 1: Substance IDs and properties for relevant substances:

Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Calcium carbonate	Physical state at 20 °C and 101.3 kPa	Solid
EC Number	207-439-9	Melting point	825 °C (aragonite) 1339 °C (calcite)

Parameter	Value	Physicochemical properties	Value
CAS Number	471-34-1	Density	2.83 g/cm³ (aragonite) 2.71 g/cm³ (calcite)
IUPAC name	Calcium carbonate	Vapour pressure	-
Molecular formula	$CaCO_3$	Water solubility	0.0166 g/L (20 °C, pH = 9-9.4)
Molecular weight	100.086 g/mol	Flammability	Non-flammable
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Calcium hydroxide	Physical state at 20 °C and 101.3 kPa	solid
EC Number	215-137-3	Melting point	580 °C (1013 hPa)
CAS Number	1305-62-0	Density	2.26 g/cm³ (20 °C)
IUPAC name	Calcium dihydroxide	Vapour pressure	-
Molecular formula	$Ca(OH)_2$	Water solubility	1844.9 mg/L (20 °C, pH = 12.4)
Molecular weight	74.092 g/mol	Flammability	Non-flammable
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Calcium metasilicate	Physical state at 20 °C and 101.3 kPa	Solid
EC Number	233-250-6	Melting point	1540 °C
CAS Number	10101-39-0	Density	2.900 g/cm³
IUPAC name	Calcium metasilicate	Vapour pressure	-
Molecular formula	CaO_3Si	Water solubility	-
Molecular weight	116.16 g/mol	Flammability	-
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Calcium borosilicate	Physical state at 20 °C and 101.3 kPa	Solid (white powder)
EC Number	-	Melting point	> 1540°C
CAS Number	59794-15-9	Density	2.65g/cm^3
IUPAC name	Calcium borate silicate	Vapour pressure	-
Molecular formula	1.4 CaO.0.5 B2O3.SiO2.H2O	Water solubility	0.34 g/L
Molecular weight	180.1 g/mol	Flammability	-

Table 2: Hazard classification and labelling

Substance Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) (labelling)	No. of Notifiers (CLP inventory)	Additional classification and labelling comments	Regulatory and CLP status
4 strictly confidential calcium compounds are used as (potential) corrosion inhibitors. Best case and worst case classification of these substances are given on the right.	Not classified	-	n/a	Best case classification of the substances.	Several, but not all, substances have been REACH registered and/or have respective entries in the CLP Regulation, Annex VI. If otherwise, information was taken from the C&L inventory (if substances were notified).
	Skin Corr. 1B	H314 (Causes severe skin burns and eye damage)	n/a	Worst case classification of the substances.	
	Eye Dam. 1	H318 (Causes serious eye damage)			
	STOT SE 3	H335 (May cause respiratory irritation)			
	Resp. Sens. 1A	H334 (May cause allergy or asthma symptoms or breathing difficulties if inhaled)			
	Aquatic Acute 3	H401 (Toxic to aquatic life)			
Calcium-carbonat (CAS 471-34-1) (EC 207-439-9)	Not classified	-	1,849	1,900 notifiers did not classify the substance. Another approximately 150 notifiers classified the substance as Skin Irrit. 2 and Eye Irrit. 2, while another ~ 70 notifiers notified the more severe classification as Eye Dam. 1	REACH registered; Not included in CLP Regulation, Annex VI;
	Skin Irrit. 2	H315 (Causes skin irritations)	96		
	Eye Irrit. 2	H319 (Causes serious eye irritations)			
	Eye Dam. 1	H318 (Causes serious eye damage)	67		
Calcium dihydroxide (CAS 1305-62-0) (EC 215-137-3)	Eye Dam. 1	H318 (Causes serious eye damage)	1,084	1,084 notifiers mentioned the hazard class Eye Damage 1. Additional 868 notifiers confirmed this classification and added Skin Irrit. 2 and STOT SE 3. 852 notifiers mentioned a single classification Skin Corr. 1B.	REACH registered; Not included in CLP Regulation, Annex VI; Included in C&L inventory
	Skin Irrit. 2	H315 (Causes skin irritation)	868		
	Eye Dam. 1	H318 (Causes serious eye damage)			
	STOT SE 3	H335 (May cause respiratory irritation)			
	Skin Corr. 1B	H314 (Causes severe skin burns and eye damage)	852		
	Eye Irrit. 2A	H318 (Causes serious eye damage)	n/a	Further classifications according to REACH registration.	
	Resp. Sens. 1A	H334 (May cause allergy or asthma			

Substance Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) (labelling)	No. of Notifiers (CLP inventory)	Additional classification and labelling comments	Regulatory and CLP status
		symptoms or breathing difficulties if inhaled)			
	Aquatic Acute 3	H401 (Toxic to aquatic life)			
Calcium metasilicate (CAS 13983-17-0) (EC 237-772-5)	Not classified	-	335	335 notifiers did not classify the substance. 80 notifiers classified the substance as Eye Irrit. 2, STOT SE3, and STOT RE2. 34 additional parties classified the substances as as Eye Irrit. 2 and STOT SE3 only.	Currently not REACH registered; Not included in CLP Regulation, Annex VI;
	Eye Irrit. 2	H319 (Causes serious eye irritation)	52		
	STOT SE 3	H335 (May cause respiratory irritation)			
	STOT RE2	H373 (May cause damage to lungs)			
Calcium borosiliate (CAS 59794-15-9)				No classification information available.	Not REACH registered; Not included in CLP Regulation, Annex VI; No CLP classification notified;

APPENDIX 3.1.3: Organic corrosion inhibitors

Table 1: Substance IDs and properties for relevant substances:

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	5-methyl-1H-benzotriazol	Physical state at 20°C and 101.3 kPa	solid
EC number	205-265-8	Melting point	80-82 °C
CAS number	136-85-6	Density	Ca. 1.3 g/cm^3 (predicted)
IUPAC name	5-Methylbenzotriazole	Vapour pressure	-
Molecular formula	$C_7H_7N_3$	Water solubility	6.0 g/L (25 °C)
Molecular weight	133.15 g/mol	Flammability	210-212 °C
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Amines, N-tallow alkyltrimethylenedi-, oleates	Physical state at 20°C and 101.3 kPa	-

Parameter	Value	Physicochemical properties	Value
EC number	263-186-4	Melting point	-
CAS number	61791-53-5	Density	-

Table 2: Hazard classification and labelling

Substance Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) (labelling)	Number of Notifiers	Additional classification and labelling comments	Regulatory and CLP status
5-methyl-1H-benzotriazol (6-methylbenzotriazole) (CAS 136-85-6) (EC 205-265-8)	Acute Tox. 4	H302 (Harmful if swallowed)	36	36 notifiers notified the substance with the single hazard Acute Tox. 4.	Currently not REACH registered; Not Included in CLP Regulation, Annex VI; Included in the C&L Inventory
	Acute Tox. 4	H302 (Harmful if swallowed)	23	Additional 23 notifiers classified the substance both with Acute Tox. 4 and with three additional hazards (see left).	Included in the C&L Inventory
	Skin Irrit. 2	H315 (Causes skin irritation)			
	Eye Irrit. 2	H319 (Causes serious eye irritation)			
	STOT SE 3	H335 (May cause respiratory irritation)			
Amines, N-tallow alkyltrimethylenedi-, oleates (CAS 61791-53-5 EC 263-186-4)	Skin Corr. 1C	H314 (Causes severe skin burns and eye damage)	433		Preregistered Substance Included in the C&L Inventory
	Eye Dam. 1	H318 (Causes serious eye damage)			
	Skin Corr. 1B	H314 (Causes severe skin burns and eye damage)	Total number of notifiers: 136	State/Form: solid	
	Eye Dam. 1	H318 (Causes serious eye damage)			
	Aquatic Acute 1	H400 (very toxic to aquatic life)			
	Skin Irrit 2	H314	92		

Substance Name	**Hazard Class and Category Code(s)**	**Hazard Statement Code(s) (labelling)**	**Number of Notifiers**	**Additional classification and labelling comments**	**Regulatory and CLP status**
	Eye Dam. 2	H318			
	Aquatic Acute 1	H400			

APPENDIX 3.1.4: Phosphate-based corrosion inhibitors

Table 1: Substance IDs and properties for relevant substances:

Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	commercially available (oxyaminophosphate salt of magnesium. Mixtures of substances)	Physical state at 20°C and 101.3 kPa	Solid (odourless, white)
EC number	Multiple components	Melting point	Decomposes at T > 180°C
CAS number	Multiple components	Density	2.05-2.35 g/cm^{-3}
IUPAC name	Multiple components	Vapour pressure	-
Molecular formula	Multiple components	Water solubility	< 0.3 g/100mL
Molecular weight	Multiple components	Flammability	Not flammable
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	commercially available (aminophosphate salt of magnesium. Mixture of substances)	Physical state at 20°C and 101.3 kPa	Solid (off-white, odourless)
EC number	Multiple components	Melting point	Decomposes T > 150°C
CAS number	Multiple components	Density	2.15-2.40 g/cm^{3}
IUPAC name	Multiple components	Vapour pressure	n.a.
Molecular formula	Multiple components	Water solubility	< 0.3 g/100mL
Molecular weight	Multiple components	Flammability	Non flammable
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	commercially available (oxyaminophosphate salt of magnesium and calcium. Mixture of substances)	Physical state at 20°C and 101.3 kPa	Solid (off-white, odourless)

Parameter	Value	Physicochemical properties	Value
EC number	Multiple components	Melting point	Decomposes at T < 180°C
CAS number	Multiple components	Density	2.25-2.60 g/ cm^3
IUPAC name	Multiple components	Vapour pressure	n.a.
Molecular formula	Multiple components	Water solubility	< 0.3 g/100mL
Molecular weight	Multiple components	Flammability	Not flammable
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	commercially available (Adjusted modified strontium aluminium polyphosphate hydrate in epoxy matrix.Mixture of Substances).	Physical state at 20°C and 101.3 kPa	Powder (white, odourless)
EC number	Multiple components	Melting point	n.a.
CAS number	Multiple components	Density	2.9 g/cm^3
IUPAC name	Multiple components	Vapour pressure	n.a.
Molecular formula	Multiple components	Water solubility	0.5% w/w
Molecular weight	Multiple components	Flammability	n.a.
Parameter	**Value**	**Physico-chemical properties**	**Value**
Chemical name and composition	commercially available (Strontium aluminium poly-phosphate hydrate in epoxy matrix).	Physical state at 20°C and 101.3 kPa	Powder (white, odourless)
EC number	Multiple components	Melting point	n.a.
CAS number	Multiple components	Density	2.9 g/cm^3
IUPAC name	Multiple components	Vapour pressure	n.a.
Molecular formula	Multiple components	Water solubility	0.5% w/w
Molecular weight	Multiple components	Flammability	n.a.
Parameter	**Value**	**Physico-chemical properties**	**Value**
Chemical name and composition	Metaphosphate-based Primer (commercially available) (multiple components)	Physical state at 20°C and 101.3 kPa	Liquid (green/yellow)
EC number	Multiple components	Melting point	-

Parameter	**Value**	**Physicochemical properties**	**Value**
CAS number	Multiple components	Density	1.06 g/cm^3 [20°C]
IUPAC name	multiple components	Vapour pressure	19.998 hPa
Molecular formula	multiple components	Water solubility	Soluble in water
Molecular weight	multiple components	Flammability Flash Point	- 38.3°C

Table 2: Hazard classification and labelling

Substance Name	**Hazard Class and Category Code(s)**	**Hazard Statement Code(s) (labelling)**	**Number of notifiers**	**Additional classification and labeling comments**	**Regulatory and CLP status**
commercially available Aminophosphate salts of magnesium and aminophosphate salts of magnesium and calcium in solvent-based epoxy primers or water-based epoxy primers	Not classified	-	n/a	Information from supplier SDS	n/a (product is a mixture of substances)
commercially available (Adjusted modified strontium aluminium polyphosphate hydrate in epoxy matrix)	Not classified	-	n/a	Information from supplier SDS	n/a (product is a mixture of substances)
commercially available (Strontium aluminium polyphosphate hydrate in epoxy matrix)	Not classified	-	n/a	Information from supplier SDS	n/a (product is a mixture of substances)
Over 30 additional, strictly confidential phosphate-based substances are used as (potential) corrosion inhibitors. Best case and worst case classification of these substances are given on the right.	Not classified	-	n/a	**Best case** classification of the substances	Substances partly REACH registered and/or included in the CLP Regulation, Annex VI; if otherwise information was gathered from the ECHA C&L inventory if applicable.
	Skin Irrit. 2	H315 (Causes skin irritation)	n/a	**Worst case** classification of the substances.	
	Eye Dam. 1	H318 (Causes serious eye damage)			
	STOT SE 3	H335 (May cause respiratory irritation)			

Substance Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) (labelling)	Number of notifiers	Additional classification and labeling comments	Regulatory and CLP status
	Aquatic Acute 1	H400 (Very toxic to aquatic life)			
	Aquatic Chronic 1	H410 (Very toxic to aquatic life with long lasting effects)			
	Acute Tox. 4	H302 (Harmful if swallowed)			
Metaphosphate-based Primer (commercially available)	Flam. Liq. 3	H226 (Flammable liquid and vapour)	n/a	Supplier hazard information from related SDS for this product.	n/a (product is a mixture of several substances)
	Skin. Sens.1	H317 (May cause allergic skin reaction)			
	Aquatic Chronic 2	H411 (Toxic to aquatic life with long lasting effect)			

APPENDIX 3.1.5: Magnesium-based corrosion inhibitors

Table 1: Substance IDs and properties for relevant substances:

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Mg Rich Primer (commercially available)	Physical state at 20°C and 101.3 kPa	Liquid (silver-white, pungent odour)
CAS Number	Multiple components	Density	1.318 g/cm^3
Molecular structure	Multiple compconents	Flammability Flash Point	35°C

Table 2: Hazard classification and labelling

Substance Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) (labelling)	Number of Notifiers	Additional classification and labelling comments	Regulatory and CLP status
Mg-rich Primer	Flam. Liq. 3	H226 (Flammable liquid and vapour)	n/a	Supplier hazard information from related SDS for this product.	n/a (product is a mixture of several substances)
	Skin Irrit. 2	H315 (Causes skin irritation)			

Substance Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) (labelling)	Number of Notifiers	Additional classification and labelling comments	Regulatory and CLP status
	Eye Irrit. 2	H319 (Causes serious eye irritation)			
	Skin Sens. 1	H317 (May cause an allergic skin reaction)			
	Aquatic Chronic 2	H411 (Toxic to aquatic life with long lasting effects)			
	Acute Tox. 4	H302 (Health hazardous when swallowed) H312 (Health hazardous by skin contact) H332 (Health hazardous when inhaled)			
	Asp. Tox. 1	H304 (Can be deadly if swallowed or if it penetrates into the respiratory apparatus)			
	Flam. Liq. 2	H225 (highly flammable liquid and vapour)			
	Eye Irrit. 2	H302 (harmful if swallowed)			
	Aquatic Chronic 3	H412 (harmful to aquatic life)			

APPENDIX 3.1.6: Molybdate-based corrosion inhibitors

Table 1: Substance IDs and properties for relevant substances:

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Disodium molybdate (monoconstituent substance)	Physical state at 20°C and 101.3 kPa	Solid (crytaline, odourless)
EC number	7631-95-0	Melting point	687.0°C (anhydrous Substance)
CAS number	231-551-7	Density	2.59 g/cm^3

Parameter	**Value**	**Physicochemical properties**	**Value**
IUPAC name	disodium tetraoxomolybdate dihydrate	Vapour pressure	-
Molecular formula	$Na_2MoO_4.2H_2O$	Water solubility	654.2 g/L
Molecular weight	241. 95 g/mol	Flammability	-
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Zinc molybdate	Physical state at 20°C and 101.3 kPa	Solid (colourless)
EC number	237-377-8	Melting point	> 700°C
CAS number	13767-32-3	Density	4.30 g/cm^3
IUPAC name	Zincdioxido(dioxo)molybdenum	Vapour pressure	N/a
Molecular formula	MoO_4Zn	Water solubility	n/a
Molecular weight	225.34 g/mol	Flammability	Not flammable
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	commercially available (Zinc molybdenum orthophosphate hydrate-based primer)	Physical state at 20°C and 101.3 kPa	Powder (white, odourless)
CAS number	Multiple components	Density	3.7 g/cm^3
Molecular weight	Multiple components	Water solubility	< 0.5%

Table 2: Hazard classification and labelling

Substance Name	**Hazard Class and Category Code(s)**	**Hazard Statement Code(s) (labelling)**	**Number of notifiers**	**Additional classification and labelling comments**	**Regulatory and CLP status**
Zinc molybdate (CAS 13767-32-3) (EC 237-377-8)	Skin Irrit. 2	H315 (Causes skin irritation)	25		Currently not REACH registered; Not included in the CLP Regulation, Annex VI
	Eye Irrit. 2	H319 (Causes serious eye irritation)			
	STOT SE 3	H335 (May cause respiratory irritation)			

Substance Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) (labelling)	Number of notifiers	Additional classification and labelling comments	Regulatory and CLP status
Organic modified zinc aluminium molybdenum orthophosphate hydrate (commercially available);	Aquatic acute 1	H400 (Very toxic to aquatic life)	n/a	Information from Supplier SDS	n/a
	Aquatic chronic 1	H410 (Very toxic to aquatic life with long lasting effects)			
Three further strictly confidential molybdate compounds - “classification ranges” are given on the right	Aquatic Acute 1	H400 (Very toxic to aquatic life)		**Worst case** classification for the three substances.	The three substances are not included in the CLP Regulation, Annex
	Aquatic Chronic 1	H410 (Very toxic to aquatic life with long lasting effects)			
	Skin Irrit. 2	H315 (Causes skin irritation)			
	Eye Irrit. 2	H319 (Causes serious eye irritation)			
	Acute Tox. 4	H332 (Harmful if inhaled)			
	STOT SE 3	H335 (May cause respiratory irritation)			

APPENDIX 3.1.7: RE-based corrosion inhibitors (Cerium, Praseodymium)

Table 1: Substance IDs and properties for relevant substances:

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Praseodymium oxide	Physical state at 20 °C and 101.3 kPa	Solid
EC Number	234-845-3	Melting point	2300 °C
CAS Number	12036-32-7	Density	7.07 g/cm^3 (20 °C)
IUPAC name	Praseodymium(III) oxide	Vapour pressure	-
Molecular formula	Pr_2O_3	Water solubility	Not miscible

Parameter	Value	Physicochemical properties	Value
Molecular weight	329.81 g/mol		
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Praseodymium oxide	Physical state at 20 °C and 101.3 kPa	Solid
EC Number	243-857-9	Melting point	2183 °C
CAS Number	12037-29-5	Density	6.9 g/cm³
IUPAC name	Praseodymium(III,IV) oxide	Vapour pressure	-
Molecular formula	Pr_6O_{11}	Water solubility	Insoluble in water, only soluble in strong acid
Molecular weight	316.899 g/mol	Flammability	Non-flammable
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Cerium nitrate	Physical state at 20 °C and 101.3 kPa	Solid
EC Number	233-297-2	Melting point	57 °C
CAS Number	10108-73-3	Density	2.4 g/cm³
IUPAC name	Cerium(III) trinitrate	Vapour pressure	-
Molecular formula	$Ce(NO_3)_3$	Water solubility	> 600 g/L
Molecular weight	326.132 g/mol	Flammability	Non-flammable
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Cerium trichloride	Physical state at 20 °C and 101.3 kPa	Solid
EC Number	232-227-8	Melting point	848 °C
CAS Number	7790-86-5	Density	2.25 g/cm³ (23.6 °C)
IUPAC name	Cerium(III) chloride	Vapour pressure	-
Molecular formula	$CeCl_3$	Water solubility	1.28-1.44 kg/L
Molecular weight	246.48 g/mol	Flammability	Non-flammable
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Cerium acetate	Physical state at 20 °C and 101.3 kPa	solid
EC Number	208-654-0	Melting point	No data available
CAS Number	537-00-8	Density	No data available

Parameter	Value	Physicochemical properties	Value
Molecular formula	$(CH_3COO)_3Ce$	Water solubility	No data available
Molecular weight	317.25 g/mol	Flammability	No data available

Table 2: Hazard classification and labelling

Substance Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) (labelling)	No of Notifiers	Additional classification and labelling comments	Regulatory and CLP status
Praseodymium oxide (Pr_6O_{11}) (CAS 12037-29-5) (EC 234-857-9)	Not classified	-			
	Aquatic Chronic 4	H413 (May cause long lasting harmful effects to aquatic life)	98		
	Aquatic Acute 1	H400 (Very toxic to aquatic life)	93	Instead of notifying the substance as Aquatic Chronic 4, 93 notifiers submitted classifications as Aquatic Acute 1 and Aquatic Chronic 1.	
	Aquatic Chronic 1	H410 (Very toxic to aquatic life with long lasting effects)			
	Skin Irrit. 2	H315 (Causes skin irritation)	71	Additional 73 parties did not notify the substance for environmental hazards but for human health effects in the combinations of: - Skin Irrit. 2, Eye Irrit. 2 - Skin Irrit. 2, Eye Irrit. 2, STOT SE 3, or - Eye Irrit. 2, STOT SE 3	
	Eye Irrit. 2	H319 (Causes serious eye irritation)	73		
	STOT SE 3	H335 (May cause respiratory irritation)	38		
Praseodymium(III) oxide (Pr_2O_3) (CAS 12036-32-7) (EC 234-845-3)	Not classified	-	7	-	Not REACH registered; Not included in CLP Regulation, Annex VI; Included in C&L inventory
	Skin Irrit. 2	H315 (Causes skin irritation)	3-5	Three notifiers submitted classifications as Skin Irrit. 2, Eye Irrit. 2 and STOTT SE 3, while two parties notified the substances as Skin Irrit. 2 and Eye Irrit. 2 only.	
	Eye Irrit. 2	H319 (Causes serious eye irritation)			
	STOT SE 3	H335 (May cause respiratory irritation)			
	Aquatic Chronic 4	H413 (May cause long lasting harmful effects to aquatic life)	1	One notifier submitted a classification for	

Substance Name	**Hazard Class and Category Code(s)**	**Hazard Statement Code(s)** **(labelling)**	**No of Notifiers**	**Additional classification and labelling comments**	**Regulatory and CLP status**
				environmental hazards only.	
Cerium nitrate (CAS 10108-73-3) (EC 233-297-2)	Ox. Sol. 2	H272(may intensify fire; oxidiser)	98		
	Eye Dam. 1	H318 (causes serious eye damage)			
	Aquatic Acute 1.	H400 (very toxic to aquatic life)			
	Aquatic chronic 1	H410 (very toxic to aquatic life with long lasting effects)			
	Aquatic Chronic 3	H412 (harmful to aquatic life with long lasting effects)	3		
	STOT SE 3	H335 (may cause respiratory irritation)	5		
Cerium acetate (CAS 208-654-0) (208-654-0	Not classified	-	9		
	Skin Irrit. 2	H315 (causes skin irritation)			
	Eye Irrit.2	H319 (causes serious eye irritation)	1		
	STOT SE 3	H335 (may cause repiratory irritation)			
	Eye Dam. 1	H318 (causes serious eye damage)			
	Aquatic Chronic 2	H411 (toxic to aquatic life with long lasting effects.	1		
Cerium trichloride (CAS 7790-86-5) (EC 232-227-8)	Skin Irrit. 2	H315 (causes skin irritation)	93		Registered Substance
	Eye Dam. 1	H318 (causes serious eye damage)			
	Aquatic Acute 1	H400(very toxic to aquatic life)			
	Aquatic Chronic 1	H410 (very toxic to aquatic life with long lasting effects)			
	Skin Irrit. 2	H315 (causes skin irritation)	35		
	Eye Dam. 1	H318 (causes serious eye damage)			
	STOT SE 3	H335 (May cause respiratory irritation)			

APPENDIX 3.1.8: Zinc-based corrosion inhibitors

Table 1: Substance IDs and properties for relevant substances:

Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Zinc	Physical state at 20 °C and 101.3 kPa	Solid
EC Number	231-175-3	Melting point	409 °C (Zn powder)
CAS Number	7440-66-6	Density	6.9 g/cm^3 (22 °C)
IUPAC name	Zinc	Vapour pressure	-
Molecular formula	Zn	Water solubility	0.1 mg/L (20 °C, pH = 6.93-8.57, powder form)
Molecular weight	65.409 g/mol	Flammability	Non-flammable
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Zinc phosphate	Physical state at 20 °C and 101.3 kPa	Solid
EC Number	231-944-3	Melting point	846 °C (1013 hPa)
CAS Number	7779-90-0	Density	3.26 g/cm^3 (22 °C)
IUPAC name	Trizinc bis(orthophosphate)	Vapour pressure	-
Molecular formula	$Zn_3(PO_4)_2$	Water solubility	2.7 mg/L (20 °C, pH ≈ 7)
Molecular weight	386.167 g/mol	Flammability	-

Table 2: Hazard classification and labelling

Substance Name	**Hazard Class and Category Code(s)**	**Hazard Statement Code(s) (labelling)**	**No. of Notifiers (CLP inventory)**	**Additional classification and labelling comments**	**Regulatory and CLP status**
Zinc Phosphate (CAS 7779-90-0) (EC 231-944-3)	Aquatic Acute 1	H400 (Very toxic to aquatic life)	n/a	-	REACH registered; Included in CLP Regulation, Annex VI (index number 030-011-00-6); Included in CoRAP-list (Initial Grounds of concern: Exposure/Wide dispersive use; Aggregated tonnage Status: Ongoing);
	Aquatic Chronic 1	H410 (Very toxic to aquatic life with long lasting effects)			
Zinc	Pyr. Sol. 1	H250 (Catches fire spontaneously			

Substance Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) (labelling)	No. of Notifiers (CLP inventory)	Additional classification and labelling comments	Regulatory and CLP status
(CAS 231-175-3) (EC 7440-66-6)		if exposed to air)			REACH registered; Harmonised classification , Annex VI
	Water-react. 1	H260 (In contact with water releases flammable gases which may ignite spontaneously)			
	Aquatic Acute 1	H400 (Very toxic to aquatic life)			
	Aquatic Chronic 1	H410 (Very toxic to aquatic life with long lasting effects)			
Zinc phosphate (CAS 231-944-3) (EC 7779-90-0)	Aquatic Acute 1	H400 (Very toxic to aquatic life)			REACH registered; Harmonised classification , Annex VI
	Aquatic Chronic 1	H410 (Very toxic to aquatic life with long lasting effects)			

APPENDIX 3.2: Electrocoat primer technology

Substance IDs and properties for relevant substances:

> The substance identity and composition of the electrocoating formulation used in the process is not known as this is proprietary of the supplier.

Hazard classification and labelling:

> The substance identity and composition of the electrocoating formulation used in the process is not known as this is proprietary of the supplier. The classification of a commercial product was reported by the supplier during the consultation as Eye Irrit. 2, and Aquatic Chronic 3 as well as Skin Irrit. 2, respectively.

APPENDIX 3.3: SILANE-BASED PROCESSES INCLUDING Sol-gel coatings

Table 1: Substance IDs and properties for relevant substances

Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Methyl trimethoxysilane (MTMS)	Physical state at 20°C and 101.3 kPa	liquid
EC number	214-685-0	Melting point	< -77 °C
CAS number	1185-55-3	Density	0.96 g/cm³ (20°C)
IUPAC name	trimethoxy(methyl) silane	Vapour pressure	7.84 hPa (20°C)
Molecular formula	$C_4H_{12}O_3Si$	Water solubility	29 g/L (20°C)
Molecular weight	136.05 g/mol	Flammability Flash point	- 11.5 °C (1013 hPa)
Parameter	**Value**	**Physicochemical properties**	**Value**
Chemical name and composition	Vinyl trimethoxysilane (VTMS)	Physical state at 20°C and 101.3 kPa	liquid
EC number	220-449-8	Melting point	-97 °C
CAS number	2768-02-7	Density	0.97 g/cm³ (20 °C)
IUPAC name	Ethenyl(trimethoxy)silane	Vapour pressure	920 Pa (20 °C)
Molecular formula	$C_5H_{12}O_3Si$	Water solubility	9.4 g/L (20 °C, pH = 7)
Molecular weight	148.05 g/mol	Flammability Flash point	- 24 °C

Table 2: Hazard classification and labelling

Substance Name	**Hazard Class and Category Code(s)**	**Hazard Statement Code(s) (labelling)**	**Number of Notifiers**	**Additional classification and labelling comments**	**Regulatory and CLP status**
Best Case: Methyl trimethoxysilane (MTMS) (CAS 1185-55-3) (EC 214-685-0)	Flam. Liq. 2	H225 (Highly flammable liquid and vapour)	96	Classification of REACH registration ; notified to the C&L inventory by 96 parties. Further 93 parties classified the substance as Flam. Liq. 2 only	REACH registered; Not included in the CLP Regulation, Annex VI; Information from C&L inventory
	Skin Sens. 1	H317 (May cause an allergic skin reaction)			
	Flam. Liq. 2	H225 (Highly flammable liquid and vapour)	296	Instead of Flam. Liquid 2 and Skin Sens. 1, 296	

Substance Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) (labelling)	Number of Notifiers	Additional classification and labelling comments	Regulatory and CLP status
	Skin Irrit. 2	H315 (Causes skin irritation)		notifiers submitted the classification as specified on the left to the C&L inventory. 64 additional notifiers submitted the same classification but abstained from the classification as STOT SE 3.	
	Eye Irrit. 2	H319 (Causes serious eye irritation)			
	STOT SE 3	H335 (May cause respiratory irritation)			
	Not classified	-	11		
	Flam. Liq. 2	H225 (Highly flammable liquid and vapour)	62	One or several classification as specified on the left were notified to the C&L inventory by another 62 parties in total.	
	Flam. Liq. 3	H226 (Flammable liquid and vapour)			
	Skin Irrit. 2	H315 (Causes skin irritation)			
	Eye Irrit. 2	H319 (Causes serious eye irritation)			
	Acute Tox. 4	H302 (Harmful if swallowed)			
	Acute Tox. 4	H332 (Harmful if inhaled)			
Worst Case: Vinyl trimethoxysilane (VTMS) (CAS 2768-02-7) (EC 220-449-8)	Flam. Liq. 3	H226 (Flammable liquid and vapour)	176	Classification included in REACH registration.	REACH registered; Not included in the CLP Regulation, Annex VI; Information from C&L inventory; Included in the CoRAP list of substances: - Initial grounds of concern: Human health/Suspected sensitiser; Exposure/Wide dispersive use;
	Acute Tox. 4	H332 (Harmful if inhaled)			
	Not calssified	-	93	93 parties did not classify the substance (C&L inventory).	
	Eye Dam. 1	H318 (Causes serious eye damage)	352	352 notifiers submitted the classification as Eye Dam. 1 only.	
	Skin Irrit. 2	H315 (Causes skin irritation)	Total number of additional notifiers: 240	Additional classifications included in the C&L inventory by notifiers in	
	Eye Irrit. 2	H319 (Causes serious eye irritation)			
	STOT SE 3	H335 (May cause respiratory irritation)			

Substance Name	**Hazard Class and Category Code(s)**	**Hazard Statement Code(s) (labelling)**	**Number of Notifiers**	**Additional classification and labelling comments**	**Regulatory and CLP status**
	Asp. Tox 1	H304 (May be fatal if swallowed and enters airways)		different combinations. 32 notifiers sumitted the classification as Muta. 1B and Carc. 1B.	Worker exposure; Exposure of sensitive population; High RCR; Aggregated tonnage - Status: ongoing
	Muta. 1B	H340 (May cause genetic effects)			
	Carc. 1B	H350 (May cause cancer)			

APPENDIX 3.5: Sources of information

Information on substance identities, physicochemical properties, hazard classification and labelling are based on online data searches. All online sources were accessed between June and September 2014. The main sources are:

1. European Chemicals Agency Website: http://www.echa.europa.eu
2. Santa Cruz Biotechnology Website: http://www.scbt.com/es/
3. Chemical Book Website: http://www.chemicalbook.com/
4. Alfa Aesar Website: http://www.alfa.com/
5. Australian Government, Department of Health: http://www.nicnas.gov.au/
6. Sigma Aldrich Website: http://www.sigmaaldrich.com
7. GuideChem Website: http://www.guidechem.com/
8. READE Website: http://www.reade.com/
9. ChemSpider Website : http://www.chemspider.com/
10. World of Chemicals Website: http://www.worldofchemicals.com

Additionally, where commercially available products were assessed into the analysis of alternatives, information from safety data sheets was included.