

ANALYSIS OF ALTERNATIVES

Non-confidential report

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LIST OF ABBREVIATIONS

AfA	Application for Authorisation
AMMTIAC	Advanced Materials, Manufacturing, and Testing Information Analysis Center
AoA	Analysis of Alternatives
ASETSDefense	Advanced Surface Engineering Technologies for a Sustainable Defense
ASTM	American Society for Testing and Materials
CAS	Chemical Abstracts Service
CKS	Chrome ceramic coating
Cr(III)	Trivalent chromium
Cr(VI)	Hexavalent chromium
CSR	Chemical Safety Report
CTAC	Chromium Trioxide Authorisation Consortium
CVD	Chemical Vapour Deposition
DLC	Diamond-Like Carbon
DoD	Department of Defense
EC	European Commission
EGR	Exhaust Gas Return
EN	European Norm
ESTCP	Environmental Security Technology Certification Program
EU	European Union
F-M	Federal-Mogul
GDC	Goetze Diamond Coating
HCAT	Hard Chrome Alternatives Team
HD	Heavy Duty vehicle
HV	Vickers Hardness
HVOF	High Velocity Oxygen Fuel
ISO	International Organization for Standardization
LVD	Light Vehicle Diesel
LVP	Light Vehicle Petrol
MRD	Middle Range Diesel
OEM	Original Equipment Manufacturer
PA-CVD	Plasma-Assisted Chemical Vapour Deposition
PVD	Physical Vapour Deposition

R&D	Research and Development
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RPA	Department for Environment, Food and Rural Affairs
SDS	Safety Data Sheet
SEA	Socio Economic Analysis
SVHC	Substance of Very High Concern
TNO	Netherlands Organisation for Applied Scientific Research
TSM	Surface Treatment Mechanics, French company

GLOSSARY

Term	Definition
Adhesion	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).
Alternative	Potential alternative provided for their evaluation.
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.
Category 1 alternative	Alternative considered promising, which is either already in use at Federal-Mogul for the application in piston rings, or can be provided on a prototype scale.
Category 2 alternative	Alternative with clear technical limitations which may only be suitable for niche applications and not as a general alternative.
Category 3 alternative	Alternative which has been screened out at an early stage of the Analysis of Alternatives as it is not suitable for the application in piston rings according to company's experience.
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.
Corrosion protection	Means applied to the metal surface to prevent or interrupt oxidation of the metal part leading to loss of material. The corrosion protection provides corrosion resistance to the surface.
Counterpart	Structural zone (like assembly, component) to which a given assembly/part is fitted.
Current production part	Components required for vehicles which are in the present production at an OEM.
Diamond-like carbon	DLC coatings for piston rings can be divided into two groups. - The hydrogen-free DLC coating under the brand name of DuroGlide® is the only one which is capable for diesel engine application to meet life time expectation having a minimum coating thickness of 20 µm. Therefore in this document the term DLC or thick DLC is used to refer to this type of coating only. - Other DLC coatings can be produced with a combination of PVD and PA-CVD method. They contain hydrogen and are not suitable as a lifetime running surface coating for piston rings. Due to the maximum achievable coating thickness of 8 µm, these coatings will be referred to as "thin DLC".
Electroplating	Electroplating is forming a metal coating on the part by an electrochemical method in an electrolyte containing metal ions and the part is the cathode, an appropriate anode is used and an electrical current is applied.
Etching	Process changing surface morphology as well as removing material. This is a pre-treatment step of the process chain preparing the surface before subsequent plating. This term has significant overlap with the term pickling. As there is no clear demarcation, the term etching is used to cover both etching and pickling as chromium trioxide pre-treatment in this document.
Functional chrome plating	An industrial use, meaning the electrochemical treatment of surfaces (typically metal) to deposit metallic chromium using a solution containing chromium trioxide (amongst other chemicals), to enhance wear resistance, tribological properties, corrosion resistance in combination with other important functional characteristics.

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Term	Definition
	Process characteristics are closed loop processing, high speed, flexibility in size, plating of inner surfaces, low process temperature, surface can be machined, assemblability. Functional chrome plating may include use of chromium trioxide in pre-treatment and surface deposits unlimited in thickness but typically between 2 µm and 5,000 µm.
Groove	The expressions first, second and third groove refer to the position of the rings of a ring package on the piston. First groove refers to the top ring, second groove to the middle ring and third groove to the bottom ring.
Implementation	After having passed qualification and certification, the third step is to implement or industrialize the qualified material or process in all relevant activities and operations of production, maintenance and the supply chain.
Legacy part	A legacy part shall mean any part of an end product 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 which is designed in accordance with a specific development contract signed before the earliest sunset date, and including all production, follow-on development, derivative and modification program contracts, based on that development program.
Main treatment	The main treatment, functional chrome plating using chromium trioxide, occurs after the pre-treatment and before the post treatment.
Metallic chrome coating	Resulting coating layer of the functional chrome plating process.
Past model service parts	Parts used for vehicles that are not produced anymore but are still on the road.
Pickling	Pickling is the removal of oxides or other compounds from a metal surface by chemical or electrochemical action. The term pickling is not used consistently within the surface finishing industry and is often referred to as the following processes: cleaning, scale removal, scale conditioning, deoxidizing, etching, and passivation of stainless steel. This term has overlap with the term Etching.
Plating	Electrolytic process that applies a coating of metal on a substrate.
Post-treatment	Post-treatment processes do not involve chromium trioxide and are performed after the main functional chrome plating process.
Pre-treatment	Pre-treatment process using chromium trioxide to remove contaminants (e.g. oil, grease, dust), oxides and scale. The pre-treatment process must also provide chemically active surfaces for the subsequent treatment. (See also: Etching).
Process chain	A series of surface treatment process steps. The individual steps are not stand-alone processes. The processes work together as a system, and care should be taken not to assess without consideration of the other steps of the process. In assessing candidate alternatives for chromium trioxide, the whole process chain has to be taken into account
Physical Vapour Deposition	Coating compositions produced by Physical Vapour Deposition in use for piston rings are mainly based on chromium nitride (CrN). Therefore in this document the term PVD is used to refer to chromium nitride based PVD coatings only.
Qualification	Original Equipment Manufacturer's (OEM) validation and verification that all material, components, equipment or processes meet or exceed the specific performance requirements.

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Term	Definition
Ring package / Ring pack	Combination of the three piston rings for first, second and third piston groove as it is tailored for a specific engine.
Running surface plating	Coating of the running surface of a piston ring which is in contact with the cylinder bore surface
Side face plating	Not only the running surface but also the side faces of a piston rings can be coated. Side face plating is used in some cases wear protection for the ring side face.
Temperature change resistance / heat resistance	The ability of a coating or substrate to withstand temperature changes and high temperatures.
Tribological properties	Tribological properties relate to friction, lubrication and wear on surfaces in relative motion and are important for moving machine parts.
Wear resistance / abrasion resistance	The ability of a coating to resist the gradual wear caused by abrasion and friction.

DECLARATION

We, Federal-Mogul Burscheid GmbH, request that the information blanked out in the “public version” of the Analysis of Alternatives is not disclosed. We hereby declare that, to the best of our knowledge as of today (12.11.2015) the information is not publicly available, and in accordance with the due measures of protection that we have implemented, a member of the public should not be able to obtain access to this information without our consent or that of the third party whose commercial interests are at stake.

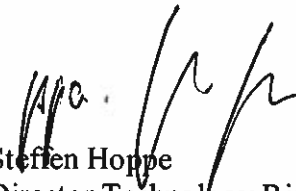
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1 SUMMARY

Introduction

This Analysis of Alternatives (AoA) forms part of the Application for Authorisation (AfA) for the use of chromium trioxide in functional chrome plating of piston rings for automotive applications at Federal-Mogul Burscheid GmbH (F-M) in the production sites in Burscheid, Dresden and Garennes-sur-Eure. The function of piston rings in combustion engines is to seal the combustion chamber against the crankcase and vice versa. Functional chrome plating of piston rings using chromium trioxide is a surface treatment process that involves depositing a layer of metallic chromium on the surface of a metallic component (e.g. ferrous materials ranging from different sorts of low-alloyed cast iron to high-alloyed chromium stainless steels, nitrided base materials). This metallic chrome coating provides the piston rings with excellent tribological properties such as high mechanical and wear resistance, and a low coefficient of friction, good machinability and the possibility to produce various designs depending on the specific needs of an engine. The process is therefore specified for particular applications where this combination of performance characteristics is critical. Functional chrome plating using chromium trioxide is therefore used for technical applications or in parts that must perform under demanding conditions that involve high temperatures, repetitive wear and mechanical impact. Approximately 360 tonnes of chromium trioxide are used in functional chrome plating within the scope of this AfA per year.

Surface treatments modify the surface of a substrate so that it performs better under conditions of use. Different chemicals and operating conditions are specified for individual plating processes in order to effectively treat different substrates and/or confer specific performance criteria to the treated article. Functional chrome plating using chromium trioxide involves immersion of the component in each of a series of treatment baths containing chemical solutions or rinses under specific operating conditions and is normally the final step in the overall surface treatment process (see **Figure 1**). Chromium trioxide is a pre-requisite for the main treatment of functional chrome plating to ensure the quality of the product and to meet the requirements of the industry. Chromium trioxide is also used in the pre-treatment process to prepare the substrate. There are no post-treatment processes for functional chrome plating which involve chromium trioxide.

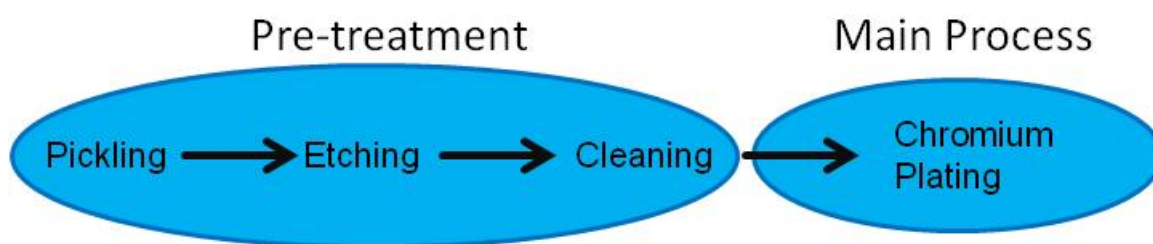


Figure 1: Simplified overview of different steps that may be involved in functional chrome plating using chromium trioxide.

The characteristics of chromium trioxide, a detailed description of the plating process, and the key functionality of the plated parts are discussed in chapter 2.

The following chapter gives an overview on the development of alternatives and subsequent approval and release processes. It also aims to specify, why the use of functional plating using chromium trioxide is necessary in order to meet the strict performance criteria for regulatory compliance, public safety and customer expectations.

Functional chrome plating with chromium trioxide

Chromium trioxide has been used for more than 50 years to provide surface protection to critical components and products within several sectors where the products to which they are applied must operate to the highest safety standards, often in demanding environments, for extended time periods. Functional chrome plating of piston rings has unique technical functions that confer substantial advantage over potential alternatives. These include:

- **Excellent tribological properties including**
- **Wear and abrasion resistance combined with hardness leading to longevity;**
- **Mechanical strength;**
- **Adequate layer thickness;**
- **Corrosion protection;**
- **Seizure resistance;**
- **Design features; and**
- **Machinability**

The chemistry behind chromium trioxide metallic chrome coatings and functional chrome plating processes is complex. As described above, chromium plating processes typically involve numerous steps, often including pre-treatment steps as well as the main treatment process itself (see **Figure 1**). These steps are almost always inter-related such that they cannot be separated or individually modified without impairing the overall process or performance of the final product. Compatibility and technical performance of the overall system are primary considerations of fundamental importance during material specification. As of today, no drop-in alternative for chromium trioxide in functional chrome plating, providing all the required properties to the surfaces of all articles in the scope of this application, is industrially available.

Furthermore, functional chrome plating using chromium trioxide has been successively refined and improved as a result of many years of research and experience at F-M, and reliable data is available to support its performance. On the other hand, data available so far for potential alternatives does not support reliable conclusions for all applications regarding their performance as part of such complex systems, in demanding environments and real-world situations. The long-term performance of such potential alternatives can currently only be estimated.

The automotive sector

F-M produces piston rings for the automotive sector for fuel and diesel engines such as Passenger Car Petrol Engines (LVP), Passenger Car Diesel Engines (LVD), Middle Range Diesel (MRD) or Truck Diesel Engines (HD). The company is a major player in piston rings for automotive applications with a global market share exceeding ■■■. In Europe F-M holds ■■■ of the market share for piston rings for gasoline engines, ■■■ for the LVD and ■■■ in the HD segment. ■■■ of F-M's piston rings are produced for engines in passenger cars and commercial vehicles regardless of usage and type of engine.

In general, piston rings fulfil the functions of sealing the combustion chamber and retaining oil outside of the combustion chamber. Piston rings differ in shape depending on the position of a specific ring within the ring package according to the respective functions. Different design features and shapes support different functional properties. If a new engine is supposed to be implemented in a vehicle model, it is necessary to validate the engine within that vehicle model, because each engine needs to receive a calibration that matches the vehicle. At first a new engine model is implemented to one vehicle model only, other engines usually follow in the subsequent years. Furthermore various derivations must be validated for several vehicle models. This procedure leads to prolonged product

life cycles, as gradually more and more vehicles are equipped with the newly developed engines. Consequently, the application of a piston ring model in the engine factory of an automotive manufacturer does not end until a vehicle is no longer produced or a follow-up engine model is introduced. Moreover implementing a new coating technology for only one component part of an engine like piston rings comes with a full development/validation schedule.

With regard to both the highly complex nature of supply chains in the automotive industry and the lifetime of vehicles, planning reliability is crucial. Average life cycles of vehicles are about 22 years and include 5 years development time, 7 years of production and at least 10 years of spare part guarantee. Certain customers claim 15 years of spare part guarantee, some others even more. The opportunity to introduce changes is only possible within a certain period of time until type-approval (see **Figure 2**).

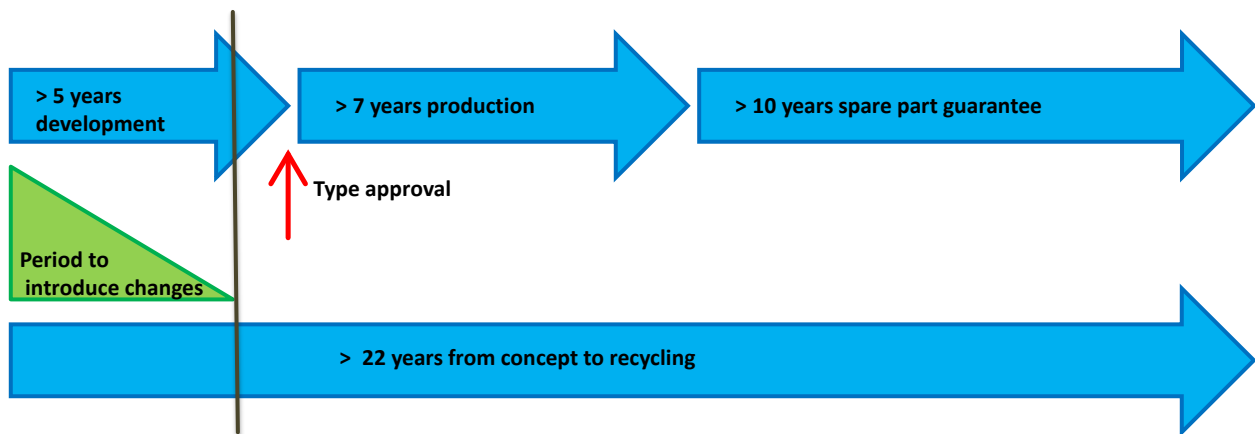


Figure 2: Typical life-time of a car model.

Additionally, functional chrome plating of piston rings is essential to reach regulatory requirements in combination with other trends new engines have to comply with, such as higher ignition pressures, higher specific loads, CO₂-emissions and particle emission in general.

Moreover, piston rings need to be designed in a way that allows the unrestricted function over the whole lifetime of a vehicle. In the automotive sector this refers to a period of 15 years, 300,000 km or 7,000 operating hours respectively. For utility vehicles the requirements are 500,000 km. For MRD engines the engine and therefore also the expected lifetime for the piston rings is 800,000 km or 8,000 – 12,000 operating hours respectively. HD and truck engines have lifetime expectations of up to 1.5 million km. To some extent these expectations have been established in order to fulfil legal requirements about structural components that effect emissions.

For these reasons, a simple one to one substitution of chromium trioxide is not possible. The identification of possible alternatives and the careful validation of their functionalities is a highly important, labour and time intensive process that will take several years. The challenge is to find a substitute to functional chrome plating with chromium trioxide which meets the requirements for all different types of products, and for the different uses of each specific application that at the same time is technically and economically feasible.

A stepwise introduction of alternative technologies in new type-approved models is planned by the automotive industry due to the magnitude of the change and impact on the industry. To make sure production volumes of vehicles are not affected, sufficient capacities for the production of alternative coatings in Europe must be confidently in place.

Federal-Mogul is strongly involved in various projects with automotive customers. Almost all projects that were launched and are still ongoing are focusing on stable conditions under special engine requirements resulting from the given environmental and customer driven targets. However, finally it is the customers who decide which design is going to be implemented in the upcoming engine generation. The decision is mainly influenced by the economic evaluation (product costs) as well as the technical advantages an alternative technology provides. Since furthermore significantly higher validation costs are connected with the introduction of a new technology, the customer/the market is only likely to change the technology, if clear advantages can be expected.

Identification and evaluation of potential alternatives

An extensive literature survey and consultation was carried out to identify and evaluate potential alternatives to chromium trioxide functional chrome plating. Eight potential alternatives were identified. Pre-treatment using chromium trioxide has been assessed separately. Five out of eight alternatives have been identified as promising alternatives, where the technique is already in use at Federal-Mogul and considerable research and development (R&D) efforts have been carried out (category 1 alternatives). These alternatives are discussed in chapter 6.1-6.5. **Table 1** at the end of this chapter summarises the main findings of the assessment of the category 1 alternatives for the use of chromium trioxide in functional chrome plating of piston rings for automotive applications. Further three out of eight alternatives showed clear technical limitations and are not subject to R&D efforts at Federal-Mogul. These (category 2) alternatives are discussed in chapters 6.6 – 6.8

In conclusion, the analysis clearly shows that there are no technically feasible alternatives to functional chrome plating with chromium trioxide for piston rings in automotive applications. Several potential alternatives are already in use at Federal-Mogul (e.g. PVD or case hardening), but only for specific applications with less critical performance requirements. They are subject to further R&D. None of these techniques fulfils all the key properties of functional chrome plating with chromium trioxide in order to eliminate the use of functional chrome plating for piston rings.

Newly developed coatings for piston ring applications such as thick DLC show promising results when comparing the performance parameters for the coating itself (e.g. wear resistance, coefficient of friction). However, these coatings are clearly no one to one substitution alternative as they cannot be used for special piston ring geometries such as sharp lower running edges, which are often used for oil control rings.

Alternatives for the pre-treatment requiring chromium trioxide are assessed separately in chapter 6.57. At the current stage, mineral acid based solutions are technically not feasible as a general alternative to chromium trioxide-based etching for all piston ring materials. Intensive research efforts are still needed to improve their performance. While an alternative for functional chrome plating is investigated, adequate custom-tailored pre-treatments are evaluated in parallel or after the potential alternatives for the main process have been qualified.

Therefore, the time needed for R&D and industrial implementation of an alternative are identical for pre-treatment and main treatment which is a minimum of 10 – 15 years.

Concluding remarks

A large amount of research over the last decades has been deployed to identify and develop viable alternatives to the use of chromium trioxide in functional chrome plating. Due to its unique functionalities and performance, it is a challenging and complex task to replace chromium trioxide-based plating in applications that demand superior tribological performance, good machinability, the possibility to produce various designs and a low coefficient of friction over extended periods and

varying environmental conditions. Several potential alternatives to functional chrome plating with chromium trioxide for piston rings are under intense investigation for the automotive sector. However, none of them is able to meet all the performance requirements of functional chrome plating for these applications.

As a result, a review period of 12 years was selected because it coincides with best case optimistic estimates by the automotive sector of the schedule required to industrialise alternatives to chromium trioxide for functional chrome plating (including pre-treatment) of piston rings for automotive applications. This time frame does not take into account the average life cycles of vehicles of about 22 years with at least 10 years of spare part guarantee.

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Table 1: Technical deficiencies of category 1 alternatives

Alternative		Reasons why alternative will not replace functional chrome plating in all applications
1	Case hardening: nitriding/nitrocarburizing	- Wear resistance insufficient for compression rings for LVD and HD - Scuff resistance insufficient for diesel and high stress petrol engines - Choice of base materials for piston rings severely limited - Sharp lower running edges not feasible due to high tendency of chipping and ring fracture
2	High velocity oxygen fuel spraying (HVOF)	- Poor adhesion of the carbides to the substrate → breaks likely to occur - Insufficient tribological behaviour on cast iron cylinders - Very hard carbide coatings on the piston rings generate massive abrasive wear on cylinder liners - Mandrel machining unavoidable - Sharp edges for oil control rings cannot be coated - Side face protection not practicable
3	Physical vapour deposition (PVD) – CrN-based	- High residual and compressive stress can negatively affect / deteriorate the piston ring shape - Sharp lower running edges for oil control rings not feasible - Side face protection not practicable - Size and number of parts that can be coated is physically limited by the need of a vacuum chamber - Experience in some engine projects show limitation of coating strength over lifetime with the result of cylinder scratches and coating damages
4	Hydrogen-free thick diamond-like carbon (DLC) coatings	- Layer thickness limited to 25 µm - Rough surface complicates machining - Sharp lower running edges for oil control rings not feasible - Side face protection not practicable - Size and number of parts that can be coated is physically limited by the need of a vacuum chamber - Immense economic burden for implementation of the process instead of functional chrome plating - Availability of production equipment extremely limited
5	Chemical vapour deposition (CVD) – thin DLC coatings	- Wear resistance inferior to high performance metallic chrome coatings like GDC - Very hard and rough surfaces require extensive post treatment of the coating - Adhesion of the coating to the substrate not as good as for functional chrome plating - Insufficient layer thickness to meet life time requirements - Size and number of parts that can be coated is physically limited by the need of a vacuum chamber - Due to brittleness and tendency to chipping sharp edge design not feasible - Side face protection not practicable

2 ANALYSIS OF SUBSTANCE FUNCTION

The present document constitutes the Analysis of Alternatives (AoA) as part of the Application for Authorisation (AfA) concerning the substance chromium trioxide, used for functional chrome plating of piston rings.

2.1 The substance

The following substance is subject to this AoA:

Table 2: Substance of this AoA.

#	Substance	Intrinsic property(ies) ¹	Latest application date ²	Sunset date ³
1	Chromium trioxide, CrO ₃ EC No: 215-607-8 CAS No: 1333-82-0	Carcinogenic (category 1A) Mutagenic (category 1B)	21 March 2016	21 September 2017

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

Chromium trioxide is categorized as a Substance of Very High Concern (SVHC) and is listed on Annex XIV of Regulation (EC) No 1907/2006. Chromium trioxide is an inorganic salt based on hexavalent chromium (Cr(VI)). Adverse effects are evaluated in detail in the chemical safety report (CSR).

The following chapter will introduce basic knowledge on piston rings that is necessary for the identification of key functionalities and the assessment of possible alternatives for functional chrome plating.

2.2 Introduction to piston rings

The processes where chromium trioxide is used for functional chrome plating of piston rings for automotive applications include:

- Pre-treatment processes, such as etching, pickling, functional cleaning and
- Main treatment process: applying a metallic chrome coating on specific substrates to enhance wear resistance, tribological properties and corrosion resistance in combination with other important functional characteristics.

2.2.1 Use of piston rings

Federal-Mogul Burscheid (F-M) produces piston rings for the automotive sector for fuel and diesel engines such as Passenger Car Petrol Engines (LVP), Passenger Car Diesel Engines (LVD), Middle Range Diesel (MRD) or Truck Diesel Engines (HD).

Combustion engines (**Figure 3**) make use of the combustion of fuels like petrol or diesel for transforming chemical energy into mechanical work. The functional unit of an engine for this transformation is the piston. Chemical energy is transformed into mechanical work by the movement of the piston due to the combustion in the chamber. Depending on the distinct phases that are passed for combustion, engines can be divided into four-stroke and two-stroke types. In a four-stroke engine, four phases are passed during operation. These four strokes are intake, compression, combustion and

exhaust. During the intake, the piston moves down and concurrently an air-fuel-mix or pure air enters the chamber. In some cases fuel is injected directly into the combustion chamber. Afterwards, the piston moves up again, compressing the gas mixture. For subsequent ignition of the mixture either a spark plug or auto-ignition is used, causing a controlled combustion. The mechanical work generated by the combustion is used to keep the engine running. The combustion forces the piston to move down again and the exhaust valve opens. Combustion gases are released, allowing the process to start again. In contrast, two-stroke engines combustion cycles only encompass two phases.

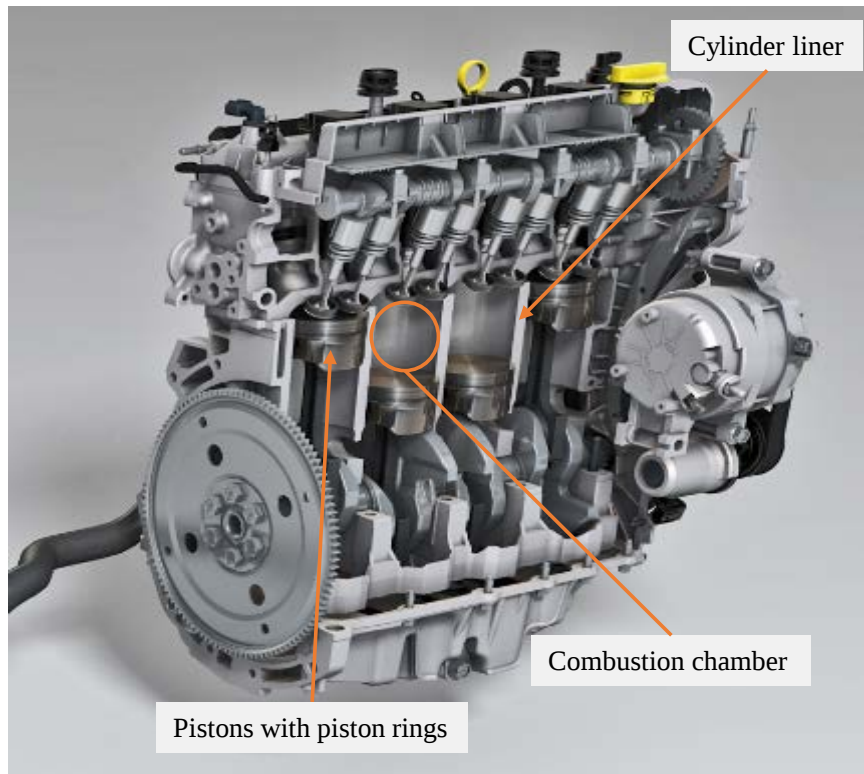


Figure 3: Interior view of an engine

For a long-lasting and reliable engine function, piston rings and cylinder liners that interact with pistons and the cylinder bore, are essential components of each engine. As illustrated in **Figure 4**, piston rings are split rings that fit into the grooves that are incorporated in the outer diameter of the piston. In combustion engines there are usually three piston rings per piston which ensure the sealing of the combustion chamber towards the crank case and vice versa.

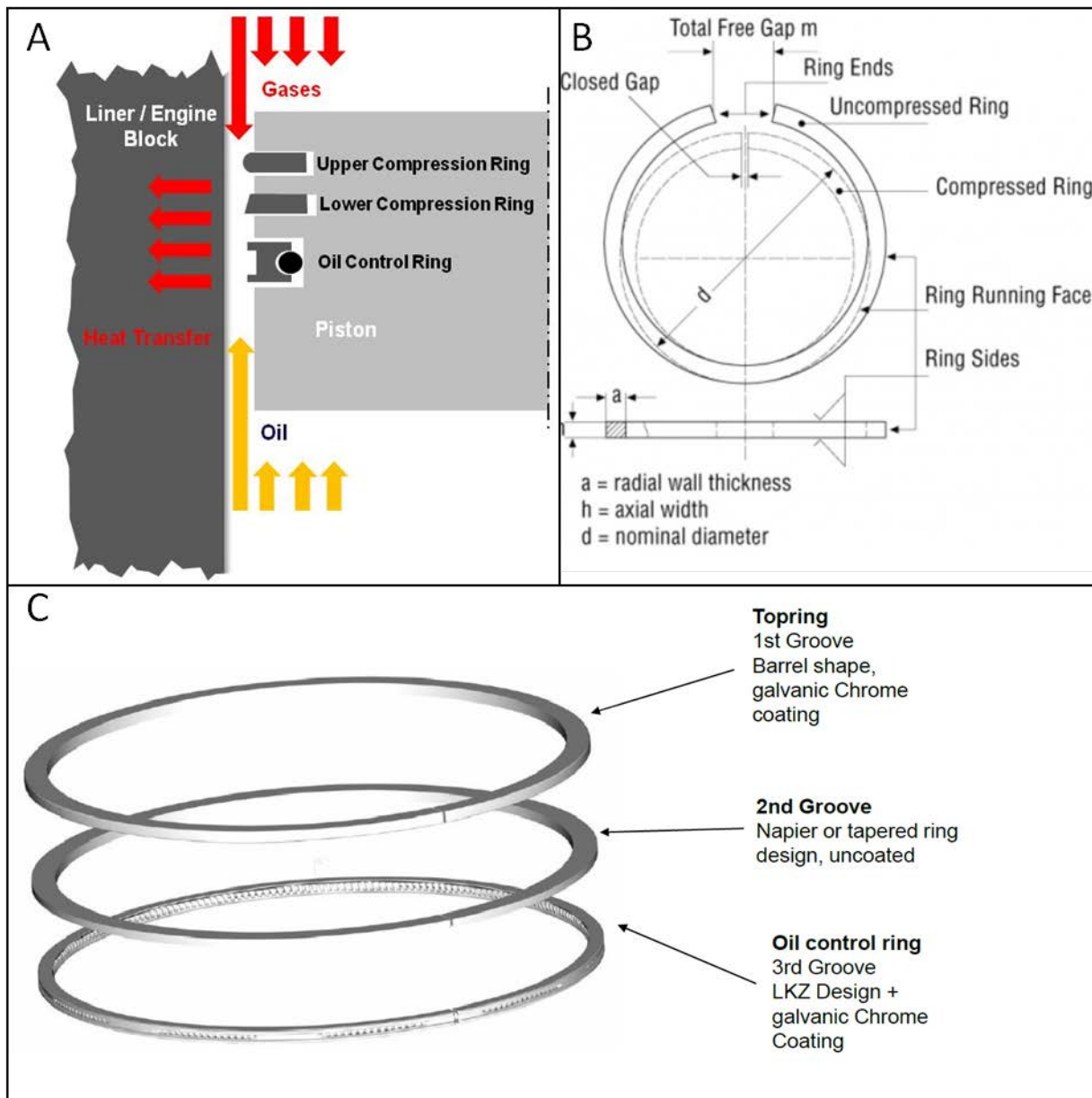


Figure 4: Illustration of piston rings (Federal-Mogul) A: piston ring B: piston rings in engine C: Example ring pack for diesel engines

2.2.2 Piston ring packages

Each of the three piston rings has its unique function which is essential for an effective operation of the whole engine. Together the three rings form a piston ring package that is tailored for the specific requirements of each specific engine.

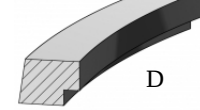
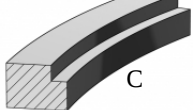
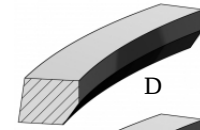
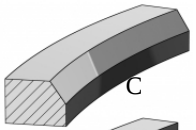
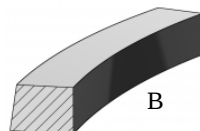
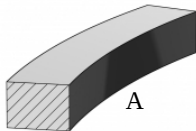
The main task of the topmost piston ring, also called “Top ring” or “1st groove ring”, is to seal the combustion chamber from the crankcase against the combustion gas. The undermost piston ring, the “3rd groove ring”, is mainly responsible for not allowing oil to get into the combustion chamber. The middle ring, the “2nd groove ring”, has a double role, which combines the roles of first and third groove.

In correlation with their function also the terms “compression ring”, “scraper ring” and “oil control ring” are commonly used.

A piston ring package is also expected to fulfil a set of additional tasks. The piston rings need to comply with the lifetime expectations of the engine. In this context parameters such as sufficient wear resistance, scuff resistance, compatibility to groove and liner and adequate blow-by control are to be ensured. Moreover piston rings are essential means which can assure that an engine works in accordance with legal requirements such as emission regulations.

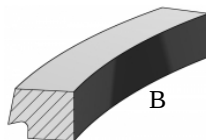
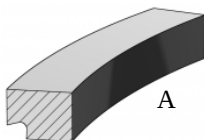
The total sum of the performance requirements (primary and additional tasks plus type of engine) is reflected in the design of each piston ring of a package and includes geometry, material and coating. Which design is chosen depends on the underlying technical and commercial conditions in the automotive segments and on the specific field-experience of engine manufacturers. Each engine is different and therefore piston ring packages need to be tailored for the specific requirements for each specific engine. **Figure 4** above gives an example for a piston ring package for a diesel engine. It is important to mention that the three rings of a ring pack are usually not of the same design.

As mentioned above, piston rings differ in the position of a specific ring within the ring package as well as in shape according to the respective function. Different design features and shapes support different functional properties. **Figure 5** gives a non-exhaustive overview of possible shapes. It has to be noted that one shape may be used in different positions within the piston ring package.



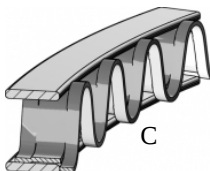
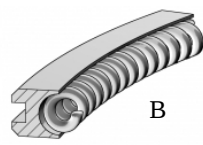
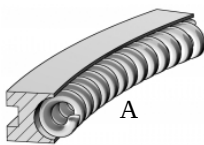
The main functions of **compression rings** are to seal the combustion chamber from the crankcase and transfer heat from the piston to the cylinder. However, they also play an important role in controlling engine oil consumption. Examples are:

- A) Rectangular ring
- B) Taper faced ring
- C) Internally Bevelled or Stepped Ring
- D) Taper faced ring with inside bottom bevel or step



Practically all of the **scraper rings** used are rings with a step recessed into the bottom outer face. This assures extremely effective oil scraping

- A) Napier Ring
- B) Taper Faced Napier Ring



Oil control rings play a major role in regulating the oil economy of the internal combustion engine. In order to control lube oil consumption most effectively, various types of oil rings are available depending on the application.

Two-piece oil control rings consist of a cast iron or profiled steel ring and a coil spring. The spring is a cylindrical coil spring made from heat-set resistant spring steel and it acts uniformly around the whole of the ring circumference. Example are:

- A) Coil Spring Loaded Slotted Oil Control Ring
- B) Coil Spring Loaded Bevelled Edge Oil Control Ring

Three-piece oil control rings consist of two thin steel rings, known as rails (segments), and an expander-spacer which

holds the rails at the required relative axial distance while simultaneously pressing them against the cylinder wall. One example is:
C) MF System

Figure 5: Summary of piston ring functions and shapes (Source: <http://korihandbook.federalmogul.com/en>).

2.3 Purpose and benefits of the use of chromium trioxide for piston rings manufacturing processes

In general, functional chrome plating provides excellent surface properties in different kind of engines. The interactions within an engine are complex. Therefore in some applications functional chrome plating is indispensable.

Functional chrome plated piston rings are used in automotive engines, such as LVP, LVD, MRD and HD. Requirements are not only particularly high but are also constantly increasing to meet the advancing customer and regulatory demands in terms of service life, performance, fuel consumption lubricating oil consumption and emissions.

The ongoing development of engines mirrors economic and competitive factors that demand downsized engines with increased engine loads in combination with increasing environmental awareness. These targets impose great challenges for the development of engines.

As a consequence, the thermal and mechanical loads for piston rings are rising. This is particularly noticeable concerning abrasive materials which increase the wear on sliding contact surfaces of piston rings, piston grooves and cylinder running surfaces. When facing these challenges, the use of chromium trioxide has multifunctional advantages, mainly based on the characteristics of the hexavalent chromium compound. The following desirable properties of metallic chrome coatings produced from chromium trioxide have made this compound a state of the art substance for piston ring coatings over several decades. The beneficial properties are:

- **Tribological behaviour**
- **Excellent wear and abrasion properties combined with hardness leading to longevity**
- **Mechanical strength**
- **Adequate layer thickness**
- **Corrosion protection**
- **Seizure resistance**
- **Design features**
- **Machinability**

Although chromium trioxide is used in functional chrome plating processes, **no chromium trioxide residues are present on the functional chrome plated article**. Indeed, this is in compliance with EU Directive 2000/53/EG on end-of-life vehicles.

To meet the increasing requirements, Federal-Mogul carried out extensive research and holds several patents for refined technologies for functional chrome plating with improved functional properties. The company developed the CKS® coating (chromium coating with aluminium oxide), the GDC® coating (chromium coating with diamond particles). These two variations are provided by F-M next to the classical chrome coating of piston rings (CR). Those coating technologies are used for piston rings for diesel engines of passenger cars and trucks. A further development based on CKS® and

GDC® technology resulted in structured chrome coatings (SCKS® and SGDC®). SCKS, for example, is a structured chromium coating with CKS on top. With this technology it is possible to provide tailor-made surface solutions.

Besides the refined chromium based technologies, F-M also tested several alternatives to the chromium surface with the aim to substitute chromium trioxide. Some of them are already used by F-M for the production of piston rings for specific engines. The challenge is to find substitutes which meet the requirements for the different types of piston rings that at the same time are technically and economically feasible. An alternative that might work for the first groove of a LVP engine for one original equipment manufacturer (OEM) does not necessarily work for the first groove of an LVP engine for a different OEM. The interaction of all parts of an engine has to be taken into account. The decision what kind of piston ring is used in which groove is to a large extent based on expert knowledge by engine and piston ring manufacturer and is individually made for each case. Therefore there is no “one and only” alternative solution for substituting the chrome coating of the pistons for all engines.

2.4 Surface treatment process description “functional chrome plating”

Surface treatment of metals is a complex and stepwise process in many industry sectors. For the operation of high performance surfaces in demanding environments, the use of chromium trioxide in metallic chrome coating components is mandatory to ensure quality and safety of the final product over decades.

As illustrated in **Figure 6**, there are various steps within the whole surface treatment process which involve the use of chromium trioxide. These are classified into the pre-treatment process (for an adequate preparation of the substrate for the subsequently applied process steps), and the respective subsequent process step (main process). There are no post-treatment processes for functional chrome plating which involve chromium trioxide.

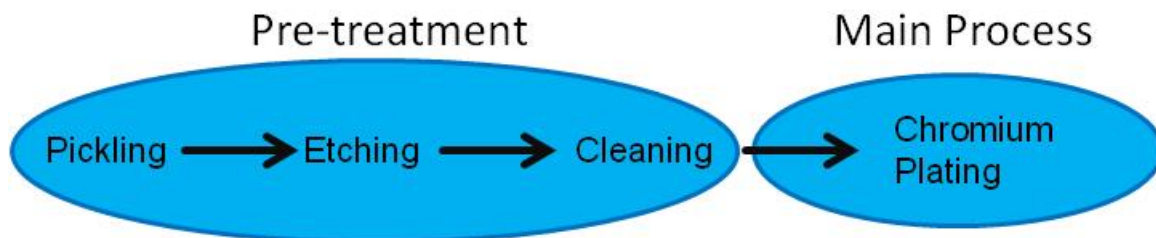


Figure 6: Simplified overview of different steps that may be involved in functional chrome plating using chromium trioxide.

It is of greatest importance that only the combination of adequate pre-treatment and the appropriate main process step leads to a well-prepared surface providing all of the necessary key requirements for the respective applications as described in detail in chapter 2.11. Chromium trioxide is a pre-requisite for the main treatment of functional chrome plating to ensure high quality of the product and to meet the requirements of the industry.

Although single process steps can be assessed individually, they cannot be seen as stand-alone processes but as part of a whole process chain. Consequently, when assessing alternatives for chromium trioxide-based surface treatments, the whole process chain and the performance of the end product must be taken into account. Indeed, although R&D on replacement technologies in surface treatments has been ongoing for decades, industry has developed and partly qualified alternate

treatments for a limited number of applications only. However, it is crucial to consider the following points:

- In each case, the performance of the alternative materials/techniques must also - and even more importantly - be evaluated as part of the whole system.
- Any change of single steps in the process chain of surface treatments will require component and/or system level test and evaluation, (re)qualification and implementation into the supply chain.
- In fact, current coating systems still typically incorporate at least one process step containing chromium trioxide.

For a thorough assessment of replacement technologies it is mandatory to include the whole process chain (including pre-treatment), taking into consideration that for **all steps** involved, chromium trioxide-free solutions must be developed, which **in combination are technically equivalent** to the current chromium trioxide-containing treatments. For the majority of functional chrome plated products at least one process step, usually the main treatment, requires chromium trioxide to provide the required properties to the surfaces.

The process description presented below covers the most relevant and critical process steps. In general, all process steps are performed by immersing the product to be plated in a bath containing the process step specific aqueous solution. It is a **wet-in-wet** process, generally without any intermediate storage of the product at any time in the process chain, except for the final drying step.

If other substances are used for the pre-treatment process than chromium trioxide, numerous rinsing steps are necessary to prevent the carry-over of solutions from the pre-treatment bath to the functional chrome plating bath, as this might lead to interferences with the respective subsequent process step and can cross contaminate the plating bath.

Base materials for piston rings are chosen for their special mechanical and wear properties. Depending on the application, they are chosen from a wide spectrum of ferrous materials ranging from different sorts of low-alloyed cast iron to high-alloyed chromium “stainless” steels. Also nitrided base materials are in use. In order to be able to choose the coating independently from the base material, both the pre-treatment and the main process must be suitable for plating all base materials with their different chemical properties so that both the coating quality and the coating adhesion fulfil the requirements.

A detailed description of the key performance parameters and the sector specific minimum requirements of the metallic chrome coating are provided in chapter 2.11. In the following chapter the process steps of functional chrome plating are described individually.

2.5 Process steps

With the establishment of machine lines and machine sections, a high level of automation has been achieved. Many of the inspection and gauging operations are integrated into the process steps. Continual process optimization and strict pre-production quality planning are a sound basis for defect-free and smooth delivery of production parts.

2.5.1 Pre-treatment processes

A number of pre-treatments are necessary to prepare the surface of the substrates for the subsequent plating process steps. For technical chromium plating of piston rings, all pre-treatment steps involve the use of chromium trioxide. Adequate preparation of the base metal is a prerequisite: adhesion

between the metallic chrome coating and the substrate depends on the force of attraction at an atomic level. Therefore, the surface of the metal must be absolutely free of contaminants, corrosion and other residuals until the plating process is finished.

Pickling is the removal of stains, inorganic contaminants and oxides like rust from a metal surface by a chemical or electrochemical process.

Pickling removes only the surface oxides. In contrast to etching, no significant amount of the underlying substrate is removed. The metal parts are dipped in a bath containing the chromium trioxide-based pickling solution. The pickling is required, as continuous oxidation during transport and manufacturing generate a natural passivation layer, making the surface less reactive to the subsequent process steps. In order to avoid rinsing steps and the creation of waste water, it is advantageous to perform pickling using a solution based on chromium trioxide.

Etching is defined as a surface activation step by removal of base material from a metal surface. The etching process creates a surface which is clean and free from defects or oxides, adequately preparing the metal surface for subsequent process steps and providing very good adhesion.

Etching affects metal surfaces in a more aggressive manner than the pickling process. For example, during a 5 minutes etching step, 2-4 μm of the substrate is removed. The removal rates vary for different substrates. Etching can be performed by immersing a metal substrate in an acidic solution. In chromium trioxide functional chrome plating, reverse etching processes using an aqueous solution of chromium trioxide are advantageous and in common use. Anodic direct current is used to increase the metal dissolution rate. As the etching action is much slower once the current stops, etching parameters and metal dissolution are very well defined for reverse etching in contrast to purely chemical etching. Chromium trioxide is necessary for controlling a moderate etch rate and to avoid over-etching. In the case of piston rings, where vastly different base materials must be pre-treated according to their chemical properties, reverse etching in chromium trioxide solution is a robust and reliable process to guarantee coating adhesion.

Reverse etching can be performed in the plating bath itself at the appropriate temperature, or in a separate etch bath. Using the plating bath saves time and space but has also disadvantages. Trivalent chromium and dissolved metal ions from substrates constantly build up within the plating bath. Over time these ions become detrimental, leading to an increase in energy consumption by decreasing the conductivity, and additionally deteriorating coating distribution and coating quality. Once a critical level of foreign metal ions is reached, the bath must be renewed. Hence, using a separate reverse etch bath is considered to be more sustainable.

Cleaning after etching: Commonly used base materials for piston rings are different sorts of cast iron, or high-alloyed chromium steels that contain carbides for wear resistance. Also nitrided base materials are in use. Virtually all of the common materials possess a structure consisting of several chemically different phases. Some of the phases, for example the graphite in the cast iron, do not dissolve during the etching process. In order to prepare the surface properly for plating and to avoid rough coatings, such undissolved material must be removed from the surface. This is done using a special cleaning step where the surface is mechanically cleaned in a chromium trioxide-based solution. It is important to use chromium trioxide as a basis because any rinsing steps between etching and plating can impair the surface activation and thus lead to faulty or badly adherent coatings.

2.5.2 Main process of functional chrome plating

The metallic chrome coating layer is applied by electroplating based on the principle of electrolysis (**Figure 7**). An optional step prior to the electroplating is a Cu or Ni-strike which is applied in some

cases for certain substrates. In this pre-step, a thin layer of few microns of Ni or Cu is applied to improve the adherence between substrate and metallic chrome coating. Additionally, thicker deposits of electroplated nickel may be used to improve the barrier corrosion performance of the coating.

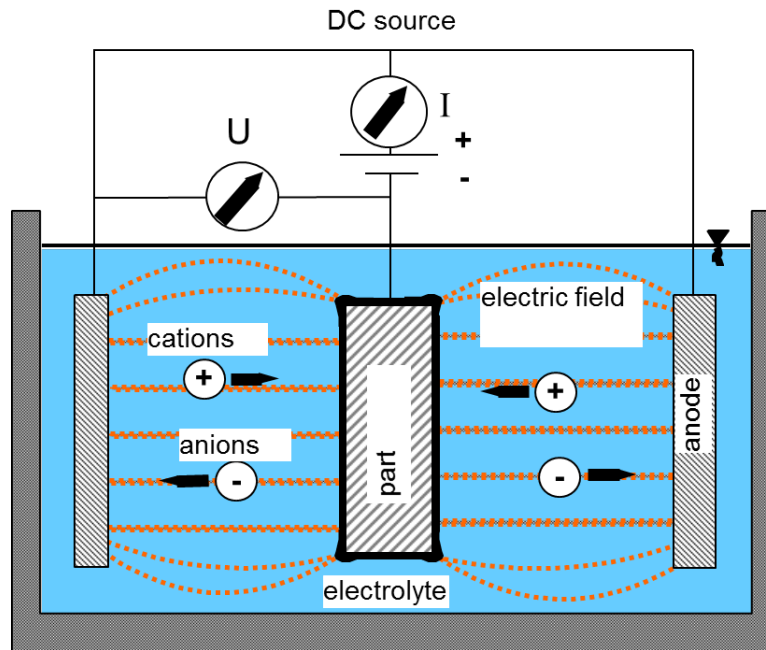


Figure 7: Principle of electroplating

During functional chrome plating a coherent metal coating forms on the part to be plated. Plating is performed either directly on the substrate or the substrate with already plated intermediate layers by using the substrate as cathode and inducing an electrical current. In chromium trioxide functional chrome plating, inert anodes are used. They often consist of platinum-coated titanium or tin-lead alloys depending on the electrolyte composition. The substrate is immersed in the electrolytic plating solution containing dissolved chromium trioxide and additives, the so-called electrolyte. During the electroplating process, the hexavalent chromium cations are reduced and build up a metallic chrome coating layer.

For chrome plating of piston rings, running surface plating has to be distinguished from side face plating. Plating of the running surface, i.e. the outer diameter of the piston ring, is much more common, as the running surface has the highest requirements in terms of wear resistance. Side face plating is performed additionally on piston rings where wear conditions are severest, for example on rings for some heavy duty or large bore engines.

Figure 8 below illustrates the principle of running surface plating of piston rings. The rings are stacked on top of each other and clamped together, forming a cylindrical mandrel. The side faces of the rings provide electrical contact over the whole length. Therefore it is not necessary to contact each single ring, nor must the inner diameter and side faces be protected from being plated. With this technique, that is very well suited to the special properties of both piston rings and the chromium trioxide functional chrome plating process, a large number of piston rings can be plated at once, making the process efficient.

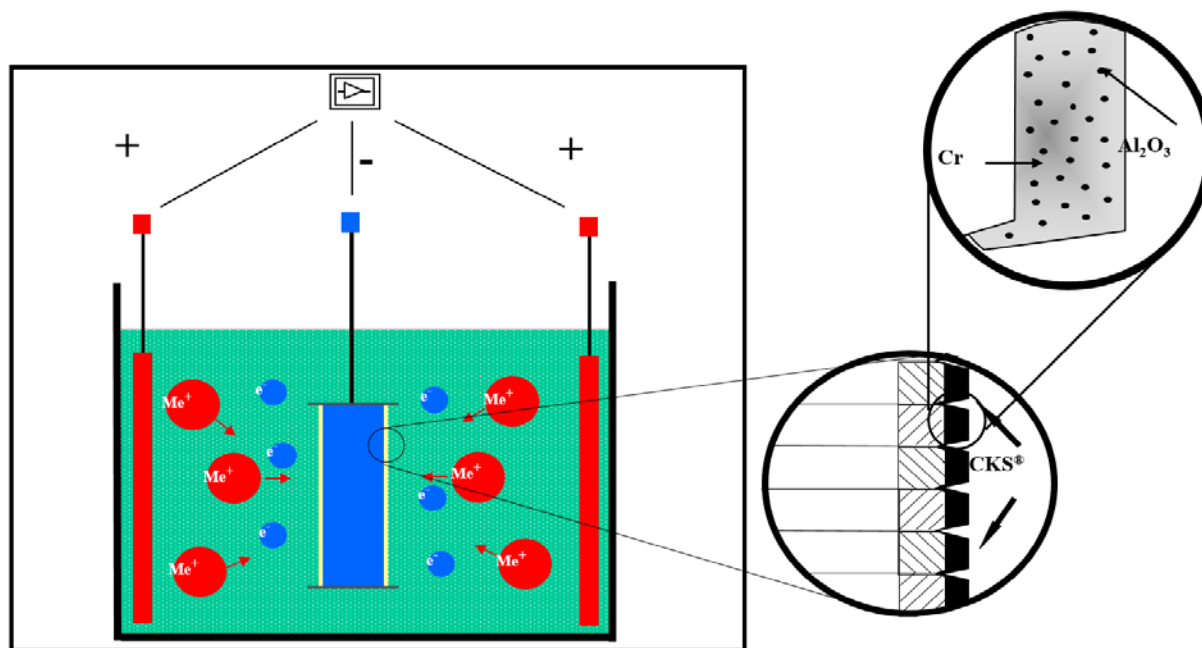


Figure 8: The electroplating process

In the plating process, solutions of chromium trioxide, with a concentration between 80 g/l and 400 g/l are used. For functional chrome plating, common concentrations are around 250 g/l. Catalysts such as sulphuric acid are added in concentrations of 1 to 5 g/l. Additional catalysts contain mixed sulphate and fluoride ions and pre-prepared proprietary catalysts with each less than 2% of the content of chromium trioxide. The sulphate bath is a commonly used chromium trioxide bath and has an efficiency of approximately 15%. Although fluoride or mixed catalysts baths have a higher efficiency than the sulphate bath (25%), their use is limited due to the chemical activity of fluoride ions which can attack the uncoated surface. Organic, often proprietary, catalysts provide higher cathodic efficiencies of up to 25% and have the advantage not to attack the uncoated base material surface in those areas of the cathodes where the current density is too low for chromium to be deposited. The current density for chromium deposition is typically in the range of 20 A/dm² to 100 A/dm².

The main side reaction is hydrogen creation. In order to prevent the aerosols from entering the inhalable air, a suitable extraction unit is indispensable.

The bath temperature usually is between 40 and 70°C. High temperatures (70°C) and solution additives reduce the number of cracks or can even eliminate them but simultaneously make the coating softer.

The properties of electrodeposited coatings depend strongly on the type and exact chemical composition of the electrolyte, the current density and the electrolyte temperature. In the case of chromium deposition, the special advantageous properties of functional chrome coatings like high hardness can only be achieved within a certain working window of electrolyte composition, current density and electrolyte temperature. The chemical properties of chromium trioxide play a crucial role in the generation of those properties. However, the exact mechanism of chromium deposition from chromium trioxide solutions is still not completely understood.

By adaptation of the plating parameters it is possible to embed particles into the micro cracks of electrodeposited chrome coatings. If the type of particles and their size is chosen properly, such coatings show much better wear resistance than pure chrome coatings. The method for incorporation

of the particles was developed and patented by Federal-Mogul. Two variants of particle-reinforced chrome coatings are currently in use: with embedded aluminium oxide (CKS) and with embedded diamond (GDC). CKS and GDC are widely used and represent a benchmark for the introduction of Cr(VI)-free coatings.

2.5.3 Rinsing, Post-treatment processes and Waste Water Treatment

As all the pre-treatment steps for chrome plating of piston rings are based on chromium trioxide, rinsing between them can be avoided. This reduces greatly the amount of waste water and contamination of the plating electrolyte and at the same time is beneficial for avoiding loss of surface activation.

Post-treatments comprise rinsing and cleaning steps to remove potentially remaining process chemicals from the product and a final drying of the product as well as grinding, lapping, polishing or thermal treatment of the functional chrome plated substrate. These post-treatments are chromium trioxide-free and are adapted depending on the component specific. However, during the rinsing process minor amounts of the plating bath concentration are accumulated in the rinsing water. Process rinsing water can therefore contain minor amounts of chromium trioxide, but this is not relevant for the cleaning process itself.

After chrome plating thorough rinsing is necessary to remove all traces of chromium trioxide from the plated piston rings.

Rinsing is commonly performed by immersing the parts in a bath filled with clean rinsing water and usually occurs in several steps (cascade technology). The most common technique is counter-current cascade rinsing, where the part is rinsed in a succession of rinsing baths that are led back to the plating bath. Modern rinsing systems reduce the water consumption by increasing the rinsing effect mechanically, for example by spraying. Most of the process water is handled in a closed-loop system minimizing waste water streams by reuse of concentrated rinsing water in the process bath of the same type. Some water evaporates and must be replenished in order to keep the bath in balance. At the same time, dragged-out electrolyte components are led back into the plating process.

For remaining water used during the rinsing process, intensive waste water treatment is required and a number of different steps of waste water treatment are known. The generated waste water streams are cleaned from chromium trioxide residues in the rinsing water by the chemical reduction to Cr(III). This is achieved under acidic conditions using reducing agents such as iron(II)sulphate. After being oxidised to trivalent iron, it serves as coagulant resulting in a precipitation with trivalent chromium in the sludge. This sludge is then disposed of. The cleaned waste water has a chromium concentration far below the thresholds of the local wastewater regulation and can be discharged to the public wastewater system.

2.6 Key functionalities of functional chrome plating of piston rings

So far the functions of piston rings in engines were explained followed by a description of the benefits of functional chrome plating of piston rings for the performance of the engine. It was also clarified how functional chrome plating works. In the following chapter key functionalities for piston rings will be introduced and criteria for the assessment of alternatives for functional chrome plating of piston rings will be identified.

An overview on the key functionalities of chromium trioxide in functional chrome plating is provided in the following chapters, subdivided into pre-treatment processes and the main coating process. Functional chrome plating can be applied on a variety of surfaces including, but not limited to steels,

stainless steels, nickel based alloys, copper alloys, aluminium alloys, titanium alloys, etc. During the consultation phase, the key functionalities for functional chrome plating were identified taking the whole surface treatment processes into account. Nevertheless, the most important key functionalities of the high-quality final product are related to the chromium trioxide-based electroplating step that results in a high-end wear resistance and hardness of the coating.

2.6.1 Key functionalities of chromium trioxide-based surface pre-treatment

The pre-treatment process prepares the surfaces for the subsequent main process step. In **Table 3**, selected key functionalities and relevant advantages for the pre-treatment process are listed and, if quantifiable, discussed in more detail below.

Table 3: Key functionalities of chromium trioxide-based pickling and etching.

Process		Key Functionality
Pre-treatment	Etching and Pickling	Well-defined, adjustable moderate etch rate
		Removal of residuals/oxides from the surface (Pickling)
		Removal of base metal substrate/oxides (Etching)
		Suitability for all piston ring base materials
		Adhesion of subsequent coatings
		Bath chemistry compatible with main process: - no contamination of subsequent baths - no rinsing steps necessary - waste water reduction - no loss of surface activation due to re-oxidation during rinsing - use of same clamping for all process steps

In order to achieve good coating quality and adhesion on all piston ring base materials, a special chromium trioxide-based cleaning step is necessary between etching and plating. Its key functionalities are listed in **Table 4** below.

Table 4: Key functionalities of chromium trioxide-based cleaning step.

Process		Key Functionality
Pre-treatment	Cleaning	Removal of undissolved structural constituents (e. g. graphite)
		Suitability for all piston ring base materials
		Adhesion of subsequent coatings
		No loss of surface activation due to rinsing between etching and plating

The key functionalities presented above are achieved by key process functionalities as presented in **Table 5**. With its optimal behaviour chromium trioxide-based pre-treatment ensures high quality products and is the decisive factor for the use of the chromium trioxide-based pre-treatment solutions.

Table 5: Key process functionalities of chromium trioxide-based pre-treatment.

Process		Key Process Functionality
Pre-treatment		Good control of etch rate and oxide removal
		Suitability for all piston ring base materials
		Sufficient surface activation to ensure coating adhesion
		Same clamping of parts usable with subsequent process step

Process	Key Process Functionality
	No detrimental contamination between subsequent baths: chemical compatibility
	Long-time bath stability
	Simple bath maintenance
	Simple analytical method for process control

Etching/ Pickling

The key functionality of etching is the adequate removal of oxide and debris from a metal surface. For etching, selective removal of certain amounts of base material is required for surface activation. This process is controlled by the **etch rate**. The careful control of this step influences the quality of the subsequent coating layer.

After the pre-treatment, the processed parts must be uniformly free of corrosion products and surface contaminations without excessive increase of surface roughness. The etching rate must be adapted according to the metal substrate used. Different types of base materials require different etching rates. A suitable pre-treatment process must be usable for all piston ring materials, as separate pre-treatment processes for different base materials would greatly increase the demand for space, equipment and efforts, for example for bath maintenance.

Under-etching or over-etching must be avoided as not to affect the key functionalities of the subsequent coating. Poor adhesion caused by under-etching, for example, could result in chipping off of the coating. The etch rate can be controlled by measuring the thickness before and after processing. Additionally, a microscopic investigation might be necessary to evaluate uniformity of the etching effect.

In order to increase bath life time and thus reduce the need of waste disposal and fresh chemicals, cross contamination between subsequent baths should be kept as low as possible. Contamination can never be avoided completely. Furthermore not every contaminating substance has the same interfering effect. Thus the chemical composition of the pre-treatment is to be chosen to lead to as little interference with the main process as possible.

Further key functionalities are the long-term use of the plating baths with proper maintenance. The bath chemicals have to be refilled ensuring dosing accuracy to prevent over- or under-etching. Additionally, the same clamping of the parts should be used in the overall process chain, reducing greatly the efforts for handling of the piston rings.

Cleaning

Virtually all piston ring materials possess a structure consisting of several chemically different phases. Some of the constituents, for example the graphite in cast iron, do not dissolve during the etching process and must be removed from the surface prior to plating. This is achieved by the cleaning step. In order not to lose surface activation, the piston rings must be transferred to the plating step as quickly as possible. This makes the use of the same clamping indispensable. Rinsing should be as much reduced as possible to prevent re-oxidation of the surface. Therefore chemical compatibility between the final pre-treatment step and the main process is very important to avoid contamination of the plating bath.

2.6.2 Key functionalities of metallic chrome coatings for piston rings

A non-exhaustive overview on requirements concerning properties and performance of chromium trioxide for functional chrome plating on piston rings is provided in **Table 6**. The key functionalities, which have been identified to be most relevant for the purpose of the product and which are essential to evaluate potential alternatives are evaluated in detail in chapter 6 below.

Table 6: Key functionalities of metallic chrome coatings of piston rings

Quantifiable key functionality	Definition / Justification	Criteria ¹
Coefficient of friction	Rig test result	0.04 – 0.05
Scuff resistance	Scuff test result in rig test	110 min
Wear resistance	Engine test	1st ring 2nd ring 3rd ring LVP <20 µm/1000h LVD, HD <25 µm/1000h <10 µm/1000h <10 µm/1000h <30 µm/1000h
Liner wear	Engine test	LVP & LVD: in general very low HD: < 6 µm / 1000h
Hardness	Hardness test	850-1,200 HV 0.1
Machinability	Necessary to achieve form needed for function, influenced by coating hardness, brittleness, roughness as plated	Good machinability, all designs possible
Adhesion of coating to substrate	Prevents chipping off during machining and operation	Adhesion should be greater than cohesion within coating and base material. No bonding problems in fired engines.
Layer thickness	Limited by internal stress, deformation, delaminating, deposition time	typically >10 µm
Corrosion resistance	Porosity, chemical composition	Resistance towards acid condensates containing nitric acid and/or sulphuric acid
Geometry/ Edge Design	Brittleness, Adhesion, batch size for vacuum process	Full face, semi inlaid Sharp bottom edge, Napier designs, Taper faced napier, Lands tapered with cylindrical land stepped, Lands tapered rounded design
Side face protection	Possibility to produce side face coatings for piston rings	Possible with functional chrome plating
Process temperature	Must not have negative effects on the quality of the coated substrate	Very low < 80 C°

¹ Generally valid for piston rings for automotive applications if not stated otherwise

Wear resistance/ Liner wear

Wear resistance describes the ability of a coating to resist the gradual wearing caused by abrasion and friction. For piston rings peripheral wear differs for each groove in different engine types the respective values are listed individually. Wear resistance can be evaluated in rig tests but always needs to be confirmed in engine tests.

High-performance functional chrome coatings with embedded aluminium oxide or diamond particles (GDC/CKS) fulfil the demands in terms of wear resistance for today's engine applications.

In addition to the wear on the piston ring running surface, wear occurs on all components which are in contact with the piston rings, like cylinder liners and piston grooves. Liner wear is especially visible and measurable in the upper turning point (top dead centre) of the piston, where the piston has a very low velocity down to zero. This results in mixed and boundary friction and therewith wear. Liner wear leads to an increased risk of scuffing, because as a consequence of wear oil depots within the liner honing will be reduced. Therefore in general the liner wear needs to be as low as possible. But it is even more important that wear rates acceptable for the system piston ring – liner are achieved. The wear rates can be optimized by the choice of an adequate piston ring coating.

Coefficient of friction

Friction is the force resisting the relative motion of solid surfaces sliding against each other. The friction coefficient is low for functional chrome plated surfaces. The coefficient of friction can be determined by tribological testing (**Figure 9**).

If one surface rubs against another under boundary conditions, the heat generated corresponds to the product of velocity, pressure and the friction coefficient. If higher friction occurs due to e.g. lack of lubrication or if the coating itself has too high friction coefficient, more heat is produced and the temperature of the coating will rise. Moreover it is important to achieve a low coefficient of friction of the coatings in order to reduce the friction loss from the asperity contact.

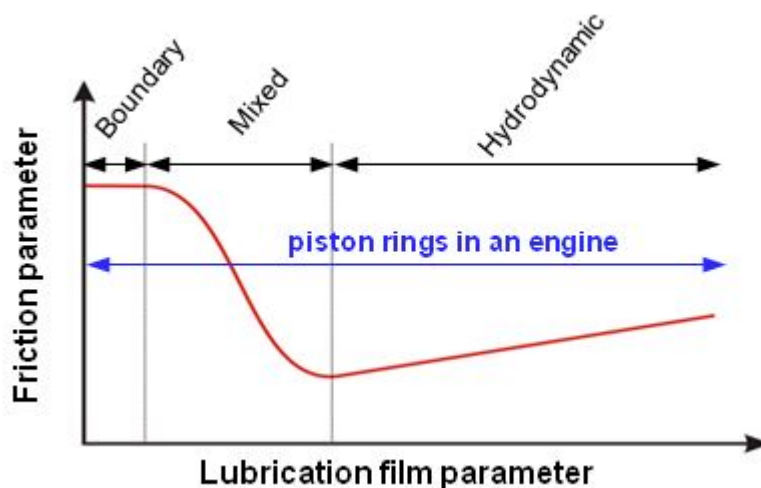


Figure 9: Schematic diagram of the Stribeck curve. During F-M rig tests, mixed friction dominates. Under tribometric testing conditions no hydrodynamic friction appears.

Scuff Resistance

Data about scuff resistance are obtained from a rig test. In this test, a piston ring segment performs an oscillating movement over a section of a cylinder liner. At the beginning of the test, a defined amount of lubricant is added. The test load increases in steps and the friction coefficient is measured. If the friction coefficient indicates seizure, the test is stopped. The test result is given as the time which a ring sample can withstand until scuffing occurs.

Hardness

Hardness is defined as the resistance of solid matter to various kinds of permanent shape changes when a force is applied. Measuring Vickers micro hardness (HV) for coatings, ISO 4516:2002, is a common hardness test method. For piston rings in the automotive sector 850-1,200 HV 0.1 is required. Hardness is linked to the scratch and abrasion resistance.

Machinability

Machinability describes which kind of finishing work is necessary or possible for a coating. Metallic chrome coatings can be characterized by their excellent machinability. They can be processed easily and allow the production of all kinds of functional design features after coating. Good machinability properties are indispensable for piston ring coatings, as piston rings can only fulfil their sealing function when the shape obtained in the production process is of adequate quality.

Adhesion of the coating to the substrate

The parameter describes the tendency of dissimilar particles or surfaces to cling to one another. For sufficient performance, neither processing steps nor engine operation must lead to a separation of the metallic chrome coating from the substrate. For chrome coatings, the adhesive forces exceed the cohesive forces within the coating and the base material.

Layer thickness

The thickness of a functional chrome plating layer varies for each application and industrial sector. Typical layer thicknesses have been identified to be typically above 10 µm but can be in a range from 5-200 µm for automotive piston rings. Thicker coatings can be applied but are not functional for automotive and HD Applications.

A sufficient layer thickness in combination with adequate wear resistance of the coating ensures that the piston ring reaches the required lifetime.

ISO 3882:2003 gives a review of methods of measurement of thickness. A common non-destructive method to determine the layer thickness of non-magnetic coatings on ferromagnetic base material is the Magnetic method, ISO 2178 & ASTM D7091. It can be used to determine the thickness of a chrome coating on all piston ring materials in use today.

Corrosion resistance

Corrosion describes the process of oxidation of a metallic material due to chemical reactions with its surroundings, especially under the effect of humidity and oxygen. In this context, the parameter corrosion resistance relates to the ability of a metal to withstand gradual destruction by chemical reaction with its environment.

For piston rings, corrosion is typically caused by acid condensates containing mainly nitric acid and/or sulphuric acid. These acids form from combustion products. Corrosive attack in automotive combustion engines is normally a secondary problem compared to mechanical wear. Therefore corrosion resistance is a desirable property of a piston ring coating, but often not the decisive factor.

Technical chrome coatings possess a good resistance against nitric acid condensates, in which they are passive. Sulphuric acid at high temperatures can destroy the passive layer, leading to strong attack of the coating.

Geometry/ Edge design

Piston rings greatly vary in design depending on the engine and their position (1st to 3rd. groove in a piston). Functional chrome plating allows manufacture of all kinds of design features and complex geometries such as sharp edges (**Figure 10**) on ring joints and running surface edges in an excellent quality.

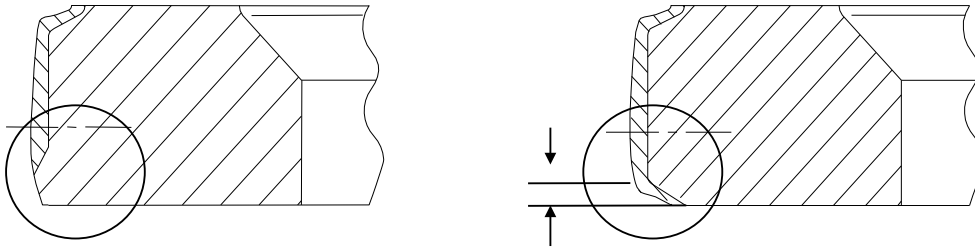


Figure 10: Cross section of piston rings: left “sharp edge design” semi inlaid with a chrome coating: right “non-machined” coating

Side face protection

Side face protection is a valuable tool to guarantee the proper function of piston rings. However it is not applied in all cases – only where it is useful to prevent side face wear. Whereas for LVP side face wear is not an issue due to state of the art piston ring base materials, for LVD engines side face wear is higher because of the generally higher stress levels in diesel engines. For piston rings for HD and MRD engines side face protection is sometimes necessary, as those engines are intended for long running lifetime which the piston rings must be suitable for.

Side face protection with functional chrome coatings is possible independently of piston ring base material. It is possible to plate either only one side face or both at the same time. Due to the low roughness of metallic chrome coatings, machining of the side faces to the required roughness is technically feasible.

Process temperature

The temperature in the functional chrome plating process is quite low. In general process temperature must not have negative effects on the quality of the coated substrate.

3 ANNUAL TONNAGE

The annual tonnage band for the use of chromium trioxide in functional chrome plating of piston rings for automotive applications per year is 360 t. An increase of the annual tonnage is not expected for the next years. Consequently the exposure and health risks are not expected to change either.

4 OVERVIEW OF THE PROCESS FOR ALTERNATIVE DEVELOPMENT AND IMPLEMENTATION IN THE AUTOMOTIVE INDUSTRY

This paragraph is intended to give an impression on the complex topic of developing and implementing an alternative coating for piston rings into the market. Different aspects are explained in this context. At first, it will be demonstrated to what extent the segments LVP, LVD, MRD and HD rely on functional chrome plated piston rings and why. Afterwards the driving forces for development at the OEMs are elucidated followed by an explanation why F-M as a component supplier does not have the power to decide which piston ring designs are implemented in the market by the OEMs. Furthermore, the timeframe and steps required for the implementation of a new technology in the automotive industry are provided. At last the issues of current production parts and past model service part is elaborated.

4.1 Market demand for functional chrome plated piston rings in the automotive sector

As of 2012, 16.2 million cars, vans, trucks buses were manufactured. Piston rings play an important role in the engines of these vehicles.

Federal-Mogul is a major player in piston rings for automotive applications with a global market share exceeding ■■■. In Europe F-M holds ■■■ of the market share for piston rings for gasoline engines, ■■■ for LVD and ■■■ in the HD segment. ■■■ of F-M's piston rings are produced for engines in passenger cars and commercial vehicles regardless of usage and type of engine. Only a small portion of about ■■■ of the piston rings produced by F-M are used in the industrial sector, such as for hydraulics and transmissions.

Federal-Mogul's Piston Ring Group serves a large number of international customers and is considered as a leader in the market. With many production sites throughout the world, closeness to the markets is assured. Short communication ways are part of the Federal-Mogul strategy. This includes the local supply of parts. For example a German OEM production receives support and products by F-M from Germany. This is why F-M maintains the production sites in central Europe, even though from the mere economic perspective locations outside Europe allow cheaper production. F-M produces piston rings for automotive application at three locations in Europe (Burscheid, Dresden, Garennes-sur-Eure).

As explained in chapter 2, a ring package is usually tailored to meet the requirements for a specific engine. F-M has defined four market segments for automotive piston rings: LVP, LVD, HD and MRD. The diagrams below (**Figure 11**) give an impression on the extent to which chromium trioxide-based coatings are currently required by OEMs for piston rings in each market segment by F-M. Additionally an outlook on the OEM requirements as expected for 2018 is provided. As explained above each of the three rings (Groove 1-3) in a liner has its specific function and therefore needs specific surface qualities. Therefore the rings are looked at separately for each segment.

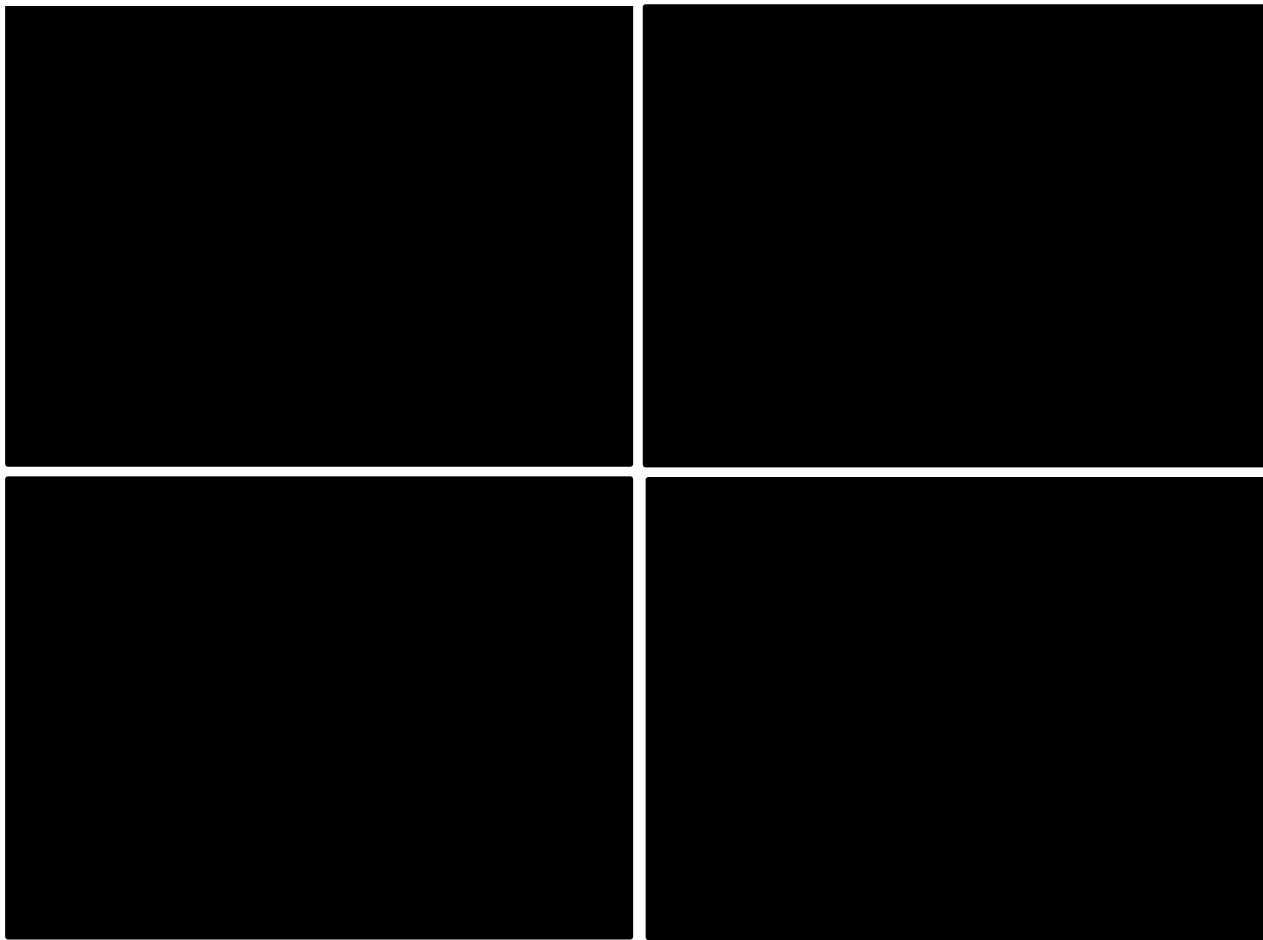


Figure 11:



A first look reveals a clear distinction between LVP and the diesel engines of LVD, HD and MRD. Functional chrome plated piston rings play a much higher role in the diesel segment. Continuously rising peak firing pressure (up to 210 bars for LVD and up to 125 bars for LVP) within the combustion chamber during compression leads to high stress levels on the components of the engine. The peak firing pressure in LVD is almost twice as high as for LVP. In order to cope with these conditions the engines need to be constructed in a more robust way. Implementation of adequate “design technology” is a valuable tool to achieve this goal. In this context the unique properties of functional chrome plated surfaces fulfil these high requirements.

Light Vehicle Petrol (LVP)

1st groove LVP: The amount of chromium trioxide-based coatings is very low. Steel rings that are either nitrided or coated by physical vapour deposition (PVD) technology are state of the art for the first groove in the LVP segment. Therefore the vast majority of piston rings in the first groove in LVP engines are not functional chrome plated. Nevertheless there are OEM clients who specifically demand functional chrome plating of the first groove for their specific engines for LVP. Some ring designs are essential for specific types of engines, as based on the current development status a specific liner and its honing may only be combined with a functional chrome plated ring. As another example there is no alternative coating applicable for asymmetric barrel shape, semi inlaid napier design rings. For other engines an alternative piston ring coating is theoretically possible, but in order

to reach regulatory requirements a special piston ring geometry may be required that can only be achieved by functional chrome plating.

2nd groove LVP: The second groove in LVP, if not functional chrome plated, is to a large extent not coated at all. Currently there is a tendency to increase the use functional chrome plated rings for the second groove. The demand for functional chrome plated rings has explicitly been expressed by customers (OEMs), who aim for more robust parts in the second groove. Market competitors push this trend as the development of downsized engines with increased power leads to higher requirements on the rings in the second groove. It also needs to be taken into account that an engine is usually designed to be implemented in vehicles world-wide. Thus the hardware components of the engines are identical. As nevertheless the conditions differ in different parts of the world the same engine is exposed to different kinds of stress. This means that requirements that are not necessary for engines in Europe may nevertheless be present in engines used outside of Europe.

3rd groove LVP: Three-piece rings that are nitrided or PVD coated are state of the art for the 3rd groove. A small percentage are two-piece uncoated piston rings. Functional chrome plated rings will be increasingly required by OEMs in 2018 compared to 2015.

Light Vehicle Diesel (LVD)

1st groove LVD: The majority of piston rings are plated with a functional chrome coating. In the next years the percentage will shift towards other technologies as F-M has just started the market launch of a new type of Cr(VI)-free DLC coating for the running surface of piston rings for the 1st groove (Duroglide®). However, the percentage of chrome coated rings is expected to remain high

2nd groove LVD: Here the majority of rings is currently plasma coated or not coated at all. Until 2018 the small percentage of chromium coated rings is expected to increase considerably. The percentage of chromium coated rings will increase in direct reply to OEM demands. Therefore in the future the rings for some applications, that today are plasma coated or uncoated rings, will then have to be chromium coated. Compared with plasma coated rings chromium coated rings show less cylinder- and self-abrasion.

3rd groove LVD: State of the art are two-piece functional chrome plated oil scraper rings. The market launch of a new type of coating for the running surface of piston rings will presumably lead to a small shift towards non-chrome plated rings

Heavy Duty (Diesel) (HD)

1st groove HD: A majority of the piston rings for the first groove in the HD segment is functional chrome plated. A small percentage is PVD coated. The percentage share of functional chrome plated piston rings is expected to decrease as a consequence of the upcoming market introduction of an alternative DLC coating method developed by F-M which has been accepted by the OEMs. The method will be discussed in detail in the chapters 5.2 and 6.15.

2nd groove HD: In this segment about half of the piston rings are functional chrome plated while the remaining rings are not plated at all. Here, no significant change is expected within the coming years.

3rd groove HD: The percentage share of functional chrome plated oil control rings for HD is expected to decrease within the next years due to the market release of the alternative DLC technology.

Middle Range Diesel (MRD):

1st and 3rd groove MRD: For MRD the 1st and 3rd groove heavily rely on the properties of functional chrome plated surfaces. Even though other coating technologies are successfully used in other types of engines, no other coating has been able to substitute functional chrome plating so far. A change is not expected for the coming years due to OEM requirements.

2nd groove MRD: Uncoated versions account for most piston rings for the second groove in MRD. The remaining number piston rings is functional chrome plated and no change in the requirements of the OEMs is expected for 2018.

Summary

The diagrams above show clearly that the rate of functional chrome plated piston rings required by the OEMs is expected to increase within the next years. There are several reasons to be mentioned in this context. Besides the requirements for piston rings with more robust running surfaces, increasing globalization of industry in general and the common-part strategy of the OEMs are responsible for this development. Automobile manufacturers usually do not produce the engines for local but for global supply (e.g. Europe, North America, China, Korea etc.). For the use of engines in countries with poor fuel quality, highly wear resistant piston rings are required. Functional chrome plated piston rings fulfil these quality requirements. Following the common-parts strategy, piston ring designs are standardized as far as possible on a global scale. Furthermore the common-parts strategy even induces the use of the same type of piston rings for diesel as well as for petrol engines. The standardization leads to an increasing demand for functional chrome plated piston rings.

4.2 Driving forces for piston ring development

As an essential part for the function of an engine the piston rings are expected to be designed in a way that allows the unrestricted function over the whole lifetime of a vehicle. In the automotive sector this refers to a period of 15 years, 300,000 km or 7,000 operating hours respectively. For utility vehicles the requirements are 500,000 km. For MRD engines the engine and therefore also the expected lifetime for the piston rings is 800,000 km or 8,000 – 12,000 operating hours respectively. Heavy Duty (HD) and truck engines have lifetime expectations of up to 1.5 million km. To some extent these expectations have been established in order to fulfil legal requirements about structural components that effect emissions.

Figure 12 gives an overview of the various driving forces for piston ring developments

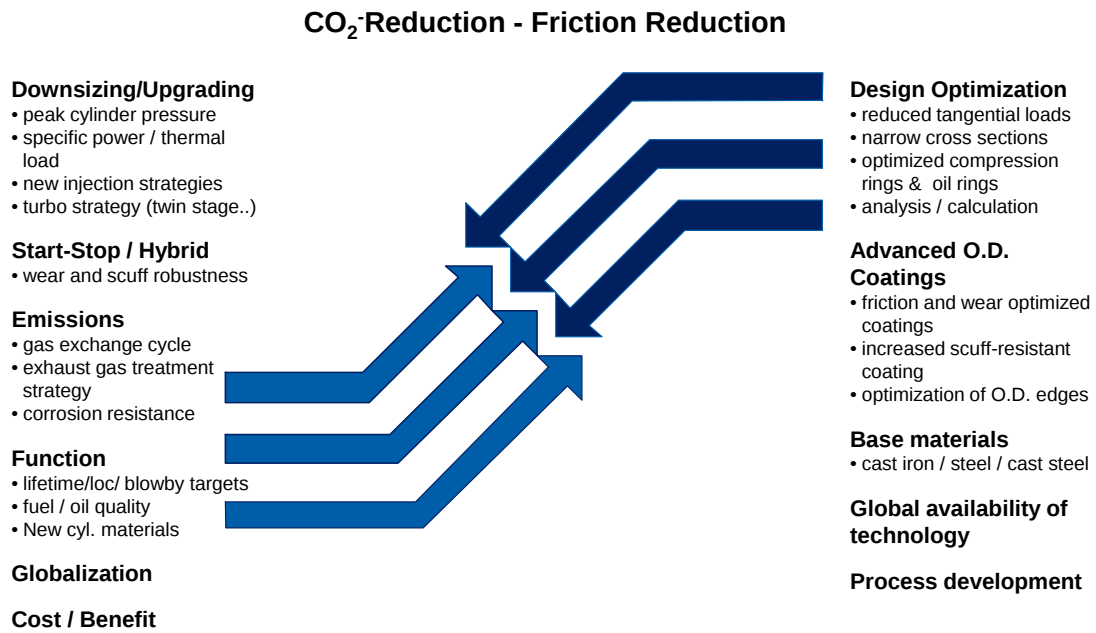


Figure 12: Key drivers for piston ring development

Piston rings are a valuable tool to optimize the energy output of an engine. The fuel-energy is not completely transformed into power output. **Figure 13** informs about the reasons for energy losses.

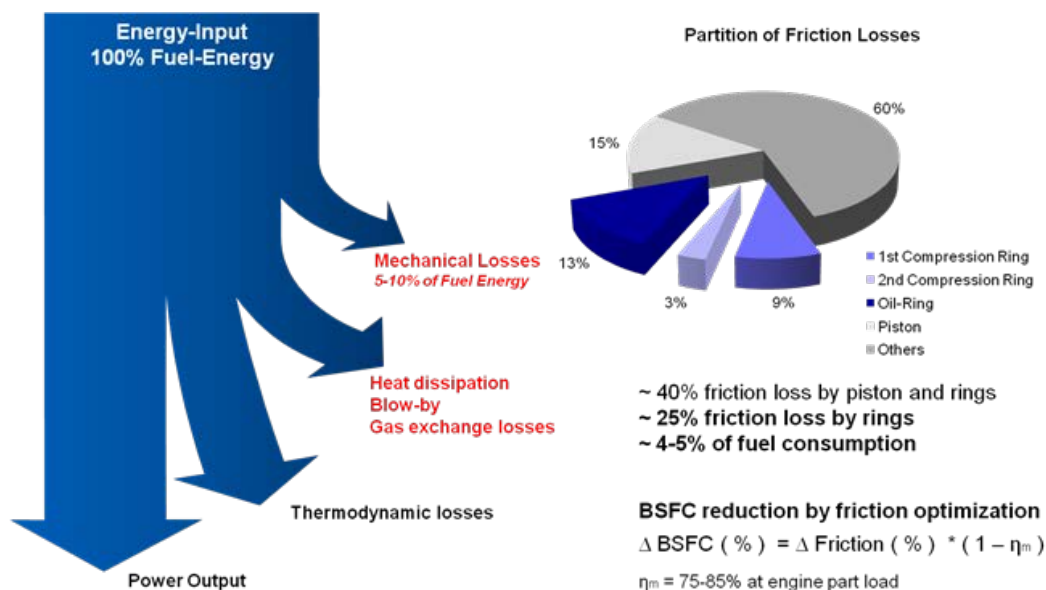


Figure 13: Reasons for energy losses in a combustion engine

The piston rings can be responsible for high rates of the losses through friction. High energy losses come along with higher fuel consumption and thus increasing CO₂-emissions. In order to reduce energy losses it is highly important to adjust the piston ring package for a specific engine as well as possible.

From a regulatory perspective the global combustion engine development is driven by the need to comply with CO₂ and particle emission regulations. It is the aim of these regulations to reduce the

emissions into the environment. In this context **Figure 14** gives an impression on the CO₂ emission targets pursued worldwide.

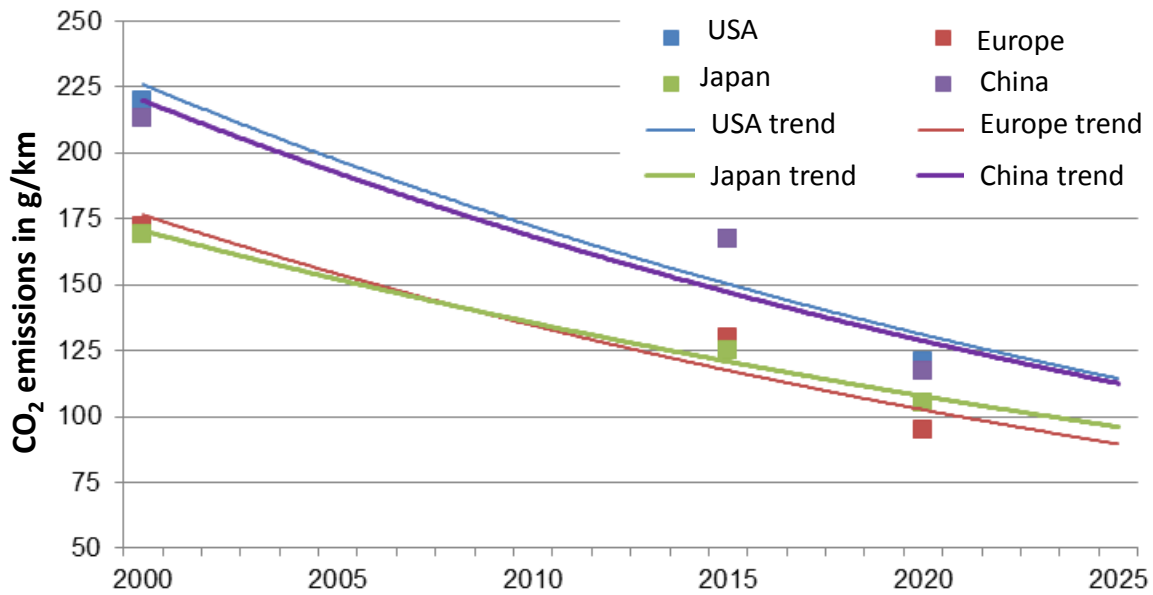


Figure 14: CO₂ emissions worldwide (Source: F-M)

Depending on the deployment region there are different regulatory standards in place across the globe such as EURO 6 for Europe, and EPA and TIER for Northern America. Additionally, in the European market self-commitment concerning corporate average CO₂ emissions.

European emission standards define the acceptable limits for exhaust emissions of new vehicles sold in European Union (EU) member states. The emission standards are defined in a series of EU directives staging the progressive introduction of increasingly stringent standards. By 2021 the CO₂-threshold of 130g/km will be decreased to 95 g/km for passenger cars (see **Figure 15** below).



Figure 15: Depiction of EU emission standards from 2012 to 2022

In the US the thresholds and directives for motor operation are set up by the Environmental Protection Agency (EPA). As OEM customers of F-M supply the non-EU market, the piston rings produced by F-M are required to meet related expectations.

Piston rings are critical parts when it comes to meeting such regulations. Theoretically the piston ring package is expected to completely seal the combustion chamber against the crankcase. As well the piston rings have to seal the crankcase and mainly the oil volume against the combustion chamber.

Those two requirements control and heavily influence the particle and emission situation of the combustion engine.

Functional chrome plating of piston rings is a valuable tool to reach these requirements concerning CO₂-emissions and particle emission in general in combination with other trends new engines have to comply with, such as higher ignition pressures and higher specific loads.

4.3 Introducing a new Technology to automotive OEMs

When a new engine model is developed, it usually starts with one vehicle type only. An automotive manufacturer will usually not exchange all precursor engine models with a new one. There is a simple reason for that: If a new engine is supposed to be implemented in a vehicle model, it is necessary to validate the engine within that vehicle model, because each engine needs to receive a calibration that matches the vehicle. As a consequence of this complex, time consuming and costly process a new engine model is implemented to one vehicle model at a time in the subsequent years only.

Furthermore an automotive manufacturer will hardly ever develop a new engine model in a single version only. Instead various derivations are designed like one with increased performance properties or a more fuel-efficient version. These derivations must be validated for several vehicle models, too.

This procedure leads to prolonged product life cycles, as gradually more and more vehicles are equipped with the newly developed engines. Consequently, the application of a piston ring model in the engine factory of an automotive manufacturer does not end until a vehicle is no longer produced or a follow-up engine model is introduced. Thereafter, the vehicle manufacturer and thus also F-M still are obligated to guarantee the supply of spare parts for 10 years.

Following Tests depict exposure/testing schedules for LVP & LVD

- ➔ Ring sticking Test (app. 200 hrs.)
 - o Engine operation with reduced axial clearance at higher load.
- ➔ Ring breakage Test (app. 200 hrs.)
 - o Engine operation with increased axial clearance at higher load.
- ➔ Hot Scuff Test (up to 50 hrs.)
 - o Green (new engine components) engines are started at ambient temperature and reduced piston clearance, and after a few seconds idling, engine is accelerated to maximum power and maximum coolant temperature.
- ➔ Cold Scuff Test (app. 10 hrs.)
 - o Same procedure as above, but under cold starting temperature.
- ➔ (Deep-) Thermal Shock (app. 2,500 cycles)
 - o In a cycling program the engine is started at cold (deep cold) temperature and warmed up with maximum power to maximum coolant temperature. After reaching the set point, the engine is stopped and rapidly cooled down to cold/deep cold temperature.
- ➔ Various Durability Tests (up to 2.500 hrs)
 - o The engine builder tries to simulate the entire engine lifetime with different kinds of durability tests.
- ➔ City Cycles (app. 1.000 hrs.)
 - o Special durability tests, simulating extreme city conditions.
- ➔ Various Vehicle Tests (up to 150.000 km)

- In addition to durability tests which take place under test bed conditions, these tests are performed in actual vehicles in harsh environments (e.g. desert, mountains, arctic, high way).
- ➔ Cold Start Test (app. 10 hrs.)
 - In a cycling program the engine is repeatedly started at deep cold temperatures for approximately 30 to 60 seconds. During these cycles, the engine stays at cold temperature.
- ➔ Start – Stop Test (app. 350.000 cycles)

The stepwise process of introducing a new or alternative coating technology for piston rings into the market is in detail provided in **Figure 16**.

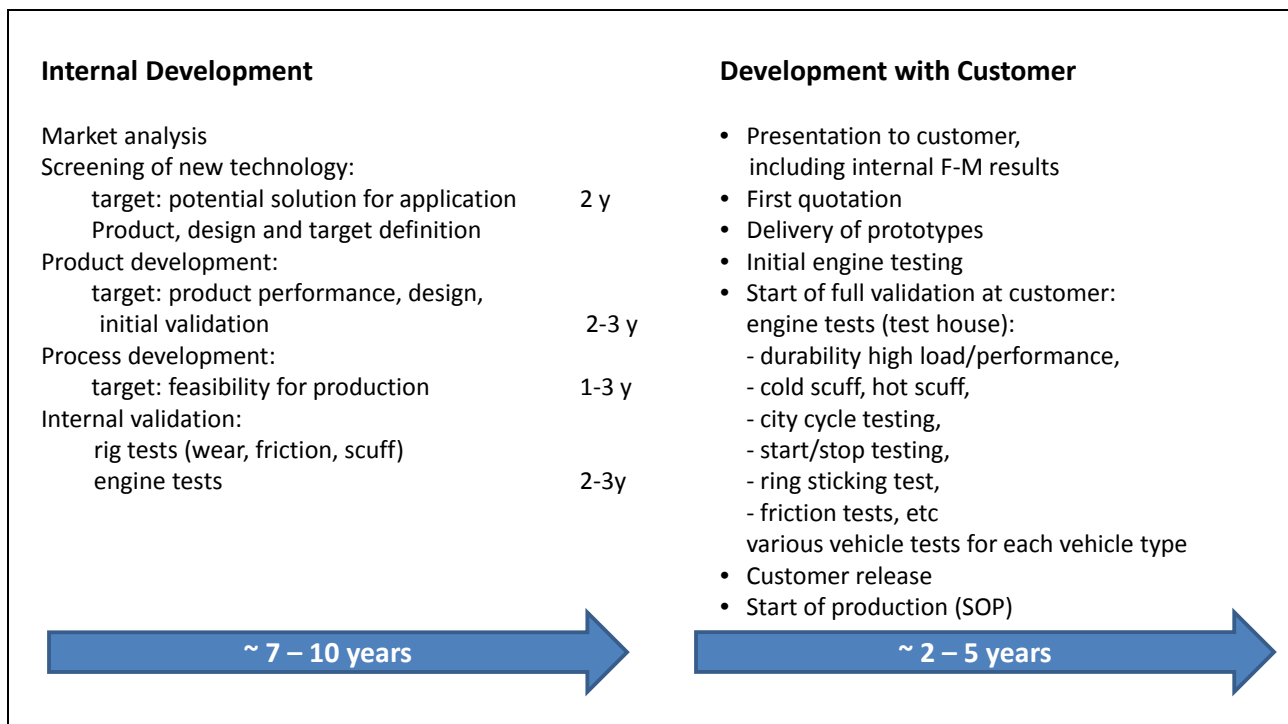


Figure 16: Implementation of a new/alternative technology for piston rings into the market

The automotive industry (customer) defines the requirements for the respective latest engine generation that is about to be developed in technical specification manuals and sheets. Thereby, F-M as a Tier 2 supplier is asked to propose ring designs, which comply with the demanded specifications. In this respect, F-M aims to differentiate from other competitors in the market, amongst other things, by offering alternative and innovative coatings technologies to their customers. However, the customers finally decide for themselves, which design is going to be implemented in the upcoming engine generation. The decision is mainly influenced by the economic evaluation (product costs) as well as the technical advantages an alternative technology provides. As significantly higher validation costs are connected with the introduction of a new technology, the customer/the market is only likely to change the technology, if clear advantages can be expected.

4.4 Current production parts

Functional chrome plated parts are unique amongst others in terms of corrosion resistance, hardness, layer thickness, adhesive strength, coefficient of friction and wear resistance. Potential alternatives must be able to cover all of these requirements. A one to one substitution is not possible and careful

testing and evaluation of an alternative's functional behaviour is needed. Current testing procedures include: laboratory tests, summer and winter tests and continuous-operation tests. Thorough evaluation of possible alternatives is crucial to avoid failures in the field / daily application. In addition to safety aspects the consequences could otherwise be expensive and highly brand damaging product recalls.

In case one substance has to be phased out or replaced, all affected components must be revalidated using suitable alternative materials. Even though the automobile industry is highly experienced in material testing procedures, the validation and testing of alternatives would most likely not be complete by the sunset date due to the sheer number of parts involved. In particular, this is the case as potential alternatives would need to be tested in terms of their extension to large scale production and be ready for use by the sunset date in September 2017.

The automotive industry deems best a stepwise introduction of alternative technologies in new type-approved models (Directives 2005/64/EC and 2009/1/EC), but this may not be feasible by sunset date.

However, to ensure production volumes of vehicles are not affected, enough capacity for the production of alternative coatings in Europe must be built up. Otherwise import from non-EU suppliers would be needed to bridge the supply gap. With EU based OEM's using 70-80% EU suppliers (and non EU based OEM's using 20-50% EU suppliers) a change to non EU suppliers would have a huge impact on the EU economy. With more than 10 million cars being built every year, building up enough capacity in Europe to cover all relevant parts is not possible within the timeframe by the sunset date.

A further point is the high complexity of supply chains in the automotive industry. The assembly of vehicles is performed in a complex network of manufacturing plants, which form a multi-tier system producing different parts, such as exterior sheets or engines. With an average number of 1,500-4,500 OEM suppliers, which have an average of 500-1,500 suppliers themselves, tracking down chromium trioxide dependent parts is a time-consuming and complicated task.

Lastly, the aforementioned multi-tier system, as well as the long-lasting nature of vehicles (up to 22 years and more) makes planning reliability crucial. Average life cycles of vehicles, are about 22 years and include 5 years development time, 7 years of production and at least 10 years of spare part guarantee. Certain customers claim 15 years of spare part guarantee, some others even more. The opportunity to introduce changes is only possible within a certain period of time until type-approval. Combining all these facts, the introduction of possible substitution parts has a long lead-time which cannot be met within the timeframe until sunset date (refer to **Figure 17**).

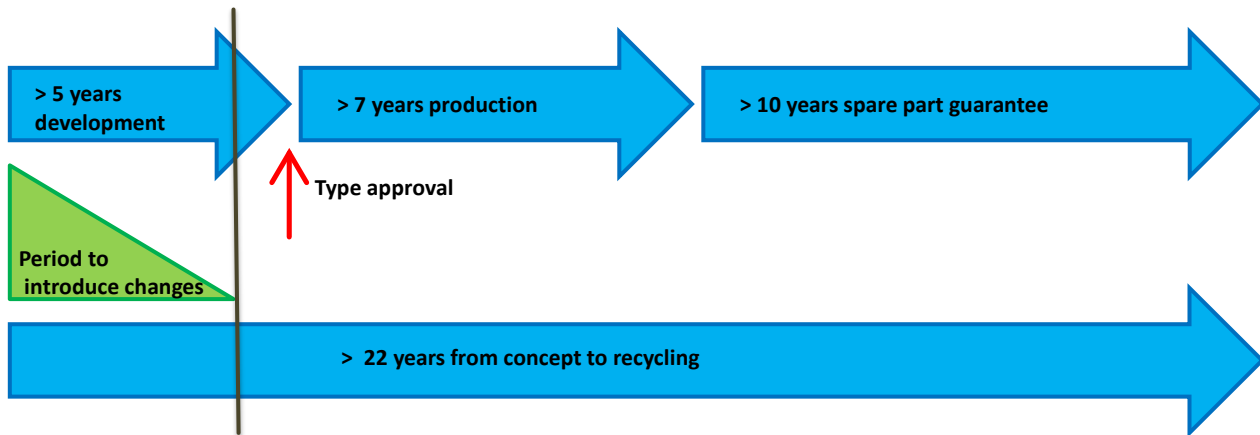


Figure 17: Typical life-time of a car model.

Implementing a new coating technology comes with a full development/validation schedule as depicted in **Figure 17** that can take up to 5 years, not having considered the necessity of new production machinery and/or manufacturing structures/processes at F-M. The period to introduce changes decreases rapidly and ends before type-approval. The time period until sunset date could affect any stage of the minimum 22 years life-time of different car models, even during the spare part period when changes are no longer possible.

4.5 Past model service parts

The EU passenger car fleet consists of about 224 million vehicles. About 36 % of the overall numbers are older than 10 years (about 80 million cars) (**Figure 18**).

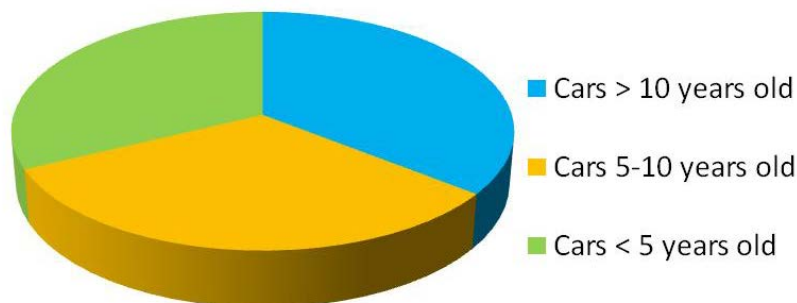


Figure 18: EU passenger car fleet (share in % by age in 2010). Note: Information from 12 EU member states where information was available.

The majority of European cars are removed from the fleet after 13 - 15 years. This underlines the importance of an efficient supply of past model service parts beyond the end of serial production. Beside service consideration, warranty obligations must be fulfilled. Therefore, a minimum of ten years availability of spare parts must be guaranteed (e.g. Germany: *Civil code §242*). Commonly, past model service parts are provided for vehicles that have been out of production for more than 20 years.

As mentioned, the interrelation of components in vehicles is highly complex and subject to thorough testing within the development phase of vehicles. Therefore, a one to one substitution of metallic chrome coatings from chromium trioxide functional chrome plating is not possible. Substance

substitution may cause change of functional geometry, thermal durability and lead to unexpected impacts on related parts. To ensure that possible alternatives are interchangeable with original spare parts, a completely new type-approval is necessary. This may lead to major disadvantages, which are discussed in the following.

Another point to be mentioned is the relatively small number of spare parts being produced. Compared to the high financial input needed for validation of alternatives, a significant increase of price per item would be the consequence.

The possibility of producing and stockpiling a sufficient amount of spare parts before sunset date should be discussed. However, this alternative may have some obvious drawbacks such as negative impacts on functionality due to chemical aging, waste of resources if spare parts are not needed for past model services, as well as high demand of stockpiling capacities.

In conclusion, the aforementioned arguments clearly show the need of metallic chrome coatings from chromium trioxide functional chrome plating in past model service part production.

5 IDENTIFICATION OF POSSIBLE ALTERNATIVES

5.1 Description of efforts made to identify possible alternatives

F-M is market leader for the supply of piston rings. As every engine has its unique characteristics, it is essential that there are specific solutions for specific needs. Customers' requests as well as the legal requirements are to be met. Therefore it is a major interest of F-M to invest in research and development of new technologies for piston ring coatings.

This AoA is based on the authorization dossier for chromium trioxide by the CTAC Consortium (Chromium Trioxide Authorisation Consortium) of 153 members that was launched in 2012. Therefore the following aspects are to a large extent adapted from that AoA (justified by a LoA).

5.1.1 Research and development

For piston rings, F-M uses a selection of high-quality cast iron and steel materials. The extensive material range covers non-alloyed, non-heat-treated special cast iron through to highly alloyed chromium steel. F-M constantly optimizes existing materials and initiates the development of new materials when required.

A large amount of research over the last 30 years has been deployed to identify and develop viable alternatives to the use of chromium trioxide for etching as well as in functional chrome plating. R&D is generally performed by testing different plated products in feasibility studies. The unique set of functionalities of chromium trioxide are explained in detail in chapter 2.11 and make chromium trioxide an ideal and not easily replaceable substance where high requirements with regard to hardness, wear resistance, corrosion, adhesion or friction, and fatigue properties have to be fulfilled to ensure safe performance in a demanding environment. It is very difficult to find an alternative which replaces the multi-functionality of chromium trioxide generated coatings.

A number of projects with the task of finding replacements for chromium trioxide generated coatings are presented below.

Ecochrom

The project Ecochrom on the "eco-efficient and high performance hard chromium process" is an Intelligent Manufacturing System-Growth project and has the objective to study and develop an environmentally and economically acceptable process allowing thick chromium coatings which are harder and more resistant to corrosion than traditional coatings, from a new and nontoxic electrolytic solution. Ecochrom is a consortium/working group of industrial platers, fundamental and applied researchers as well as end-users in Canada, USA, Japan and Korea, and is coordinated by TSM (Surface Treatment Mechanics), the main functional chrome plating specialist in France. The results of the Ecochrom project are still confidential.

The hard chrome alternatives team

The Hard Chrome Alternatives Team (HCAT), is a US-Canadian collaboration of environmental working groups of the Departments of Defence of the two nations. They pursue the objective to demonstrate and validate that the alternative High Velocity Oxygen-Fuel (HVOF) is a superior alternative to functional chrome plating. Their efforts particularly focus on the aerospace industry and on military use. Increasing time intervals between maintenance and reduced turnaround times for repair of components would lead to a more sustainable performance. However, HCAT concluded that

The Advanced Surface Engineering Technologies for a Sustainable Defense (ASETSDefense) is a US Department of Defense (DoD) initiative sponsored by the department's two environmental research programs (Strategic Environmental Research and Development Program and Environmental Security Technology Certification Program (ESTCP)). Its objective is to facilitate the implementation of more environmentally friendly technologies for surface coatings and surface treatments. This initiative wishes to provide access to background information and technical data from research, development, test, and evaluation efforts as well as the status of approvals and implementations. ASETSDefense targets defence organizations and provides information to reduce environmental safety and occupational health impacts from coatings and treatment processes that utilize e.g. chromium plating from hexavalent solutions. The database providing information on the DoD's data on authorization and implementation of alternatives is readily accessible to the public (<http://www.asetdefense.org> as of August 6, 2014).

Potential replacements of Cr(VI) have been investigated in the comprehensive “Amcoat” project in the early 2000s. The project was accomplished by an industrial group of nine companies **including F-M**, electroplaters and component producers from the UK, Denmark, Germany and the Netherlands and was supported by two scientific institutes (University of Nottingham and Netherlands Organisation for Applied Scientific Research (TNO)).

- to develop Cr(VI) free plating solutions capable of depositing amorphous metal coating,
- to demonstrate that electrodeposited amorphous coatings have at least equivalent surface properties, like hardness, wear and corrosion resistance and, low friction, as metallic chrome coatings,
- to demonstrate that operating an industrial plating plant result in an overall reduction of health and safety hazards for the workforce, reduction of environmental discharges and that it is technically and economically feasible.

Indeed, on the basis of the aforementioned unique properties and diverse functionalities of chromium trioxide and the multiple process step coating systems, alternatives have to be identified and implemented into all process steps to be completely chromium trioxide-free.

DuroGlide® is the trade name of a new kind of chromium trioxide-free coating for piston rings and has been developed by F-M itself. The hydrogen-free DLC (diamond-like carbon) coating technology has also been mentioned by the PACE Award and can be a solution as an alternative technology within the Diesel business. The milestones of development are given in the following:

- Start of Development 2008
- Basic research, Feasibility 2012

- Product and Process Development 2014
- Serial Development 2016

From the start of the development phase in 2008 until serial development in 2016 the F-M will have invested 8 years for the implementation for this new alternative coating technology. The reasons why DuroGlide® cannot substitute functional chrome plating for all piston ring applications will be discussed in chapter 6.22.

General laser and weld coating technologies

From 1988-1991 F-M conducted an extensive research project with the aim to identify potential new types of piston ring coating technologies. The project was a cooperation between the research departments of F-M and an OEM. Thus not only the feasibility of the coating process itself could be assessed, but also the resulting functionality of the piston ring coatings in an engine. Intensive testing was carried out on laser and weld coating technologies. But neither the production process nor the application in the engine revealed satisfying results, which is why development of these technologies was not pursued any further. Because of these potential alternatives were screened out by extensive research by F-M itself, the general laser and weld coating technologies will not be assessed as alternatives for functional chrome plating for piston rings within this AoA.

Hercules

The Hercules project was conceived in 2002 as a long-term R&D Programme to develop new technologies for marine engines. The project is the outcome of a joint initiative by two major European engine manufacturer groups, which together hold 90% of the world's marine engine market. The aim of this project was to:

- Increase engine efficiency, thus reduce fuel consumption and CO₂ emissions.
- Reduce gaseous and particulate emissions.
- Increase engine reliability.

Hercules C is the third Phase of the project. Hercules C ran for three years from 2012 until 2015 with a total budget of 17 million € and was partly funded by the EU.

Hercules C was conducted by six associate members from industry and university (Danmarks Tekniske Universitet, Engineered Performance Coatings, **Federal-Mogul Burscheid GmbH**, Gehring Technologies GmbH, M. Juergensen GmbH & Co KG, MAN Diesel & Turbo SE) that are specialised in the field of marine engines. F-M brought in their expertise in the field of piston ring coatings for large bore engines. Thus the following objectives were achieved successfully:

- Reducing the wear of piston rings by 10 % for two-stroke marine engines
- Reducing friction between piston ring and cylinder liner by 10 % for two-stroke and 20 % for four-stroke marine engines
- Identifying new materials and surface technologies suitable for piston ring and cylinder liner for large marine diesel engines

Summary

Although extensive research has been conducted, no one-to-one replacement to chromium trioxide or innovative technologies, which meets all the requirements, has been discovered. The final implementation of an alternative for chromium trioxide at industrial scale for key applications will therefore take a minimum of 12-15 years. This time frame does not take into account the average life cycles of vehicles of about 22 years with at least 10 years of spare part guarantee.

5.1.2 Data searches

As a basis for this AoA, the documents derived by the CTAC consortium were purchased via a Letter of Access. For this AoA, extensive literature and test reports were provided by the technical experts from Federal-Mogul to adapt and refine the document to the application of functional chrome plating of piston rings for automotive applications. Furthermore, searches for publically available documents were conducted to ensure that all potential alternate processes to chromium trioxide-containing applications were considered in the data analysis.

5.1.3 Consultations

During extensive workshops with technical experts from Federal-Mogul, an overview on the completeness and experience with the alternatives, specific processes and the minimum technical requirements for the use of functional chrome plating of piston rings for automotive applications were elaborated.

At this stage of the data analysis, some alternatives were screened out after bilateral discussions with the company, based on confirmation that they might pose a potential alternative to chromium trioxide-based processes (e.g. for functional plating with decorative character) but are not applicable for the use defined here.

To verify data and to obtain further detailed quantitative information, more focused technical questions were sent out and discussed with the experts. Moreover, a site visit to Burscheid was carried out. Final data analysis led to the formation of a list of alternatives divided into two categories, according to their potential to be suitable for the specific use defined here.

In summary, the categorized table of alternatives listed below is the outcome of extensive literature, in-house research and consultations with technical experts of Federal-Mogul.

5.2 List of possible alternatives

The most promising alternatives for chromium trioxide in functional chrome plating (**Table 7**) are assessed in detail in the following chapter 7.

According to their relevance, the potential alternatives are classified as Category 1 or Category 2. Category 1 alternatives are either already in use for the application in piston rings, or can be provided on a prototype scale. Category 2 alternatives show clear technical limitations and may only be suitable for niche applications but not as a general alternative.

An overview of the potential alternatives in each process is provided in the following table.

Table 7: List of alternatives categorized.

Category	No.	Alternative
Category 1 alternatives	1	Case hardening: nitriding/nitrocarburizing
	2	High velocity oxygen fuel spraying (HVOF)
	3	Physical vapour deposition (PVD) – CrN-based
	4	Hydrogen-free thick DLC coatings
	5	Chemical vapour deposition (CVD) – thin DLC coatings

Category	No.	Alternative
Category 2 alternatives	6	Wire flame spraying
	7	Plasma spraying
	8	Trivalent hard chromium deposition
Pre-treatment	9	Mineral acids

PVD (Physical Vapour Deposition): Coating compositions produced by Physical Vapour Deposition in use for piston rings are mainly based on chromium nitride (CrN). Therefore in this document the term PVD is used to refer to chromium nitride based PVD coatings only.

DLC (diamond-like carbon): DLC coatings for piston rings can be divided into two groups:

- The hydrogen-free DLC coating under the brand name of DuroGlide® is the only one which is capable for diesel engine application to meet life time expectation, having a minimum coating thickness of 20 µm. Therefore in this document the term DLC or thick DLC is used to refer to this type of coating only.
- Other DLC coatings can be produced with a combination of PVD and plasma-assisted chemical vapour deposition (PA-CVD) method. They contain hydrogen and are not suitable as a lifetime running surface coating for piston rings. Due to the maximum achievable coating thickness of 8 µm, these coatings will be referred to as “Thin DLC”.

6 SUITABILITY AND AVAILABILITY OF POSSIBLE ALTERNATIVES

To assess the feasibility of the alternatives, colour-coded summary tables are included in the document.

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.

The alternative assessments each comprise a non-exhaustive overview of substances used with the alternatives and alternative processes as well as the risk to human health and environment. These tables are provided in Appendix 1.

CATEGORY 1 ALTERNATIVES

The alternatives assessed in this chapter are considered the most promising, or already in use for piston rings. Each alternative offers its own advantages. They either show technical limitations when it comes to the demanding requirements, such as wear resistance and/or have economical disadvantages at the current stage. However, some of these possible alternatives are already industrialized for certain applications, but not as a general alternative. Note that the list of substances provided for each alternative is extensive but not conclusive.

6.1 ALTERNATIVE 1: Case hardening: nitriding/nitrocarburizing

6.1.1 Substance ID and properties

Nitriding/nitrocarburizing is a process used mainly for enhancing the performance of piston rings in petrol engines. The nitrided case with the resulting significant increase in hardness has the effect of reducing abrasive and adhesive wear and improving scuff behaviour compared to the un-treated base material. This technology is mainly used for petrol engines in Groove 1 and 3, where it can be considered as state of the art method.

Process description

Case hardening is a very common process that is used to harden the outer surface of metals creating a hard outer metal layer (“case”) while the deeper metallic material is unaffected, see **Figure 19**.

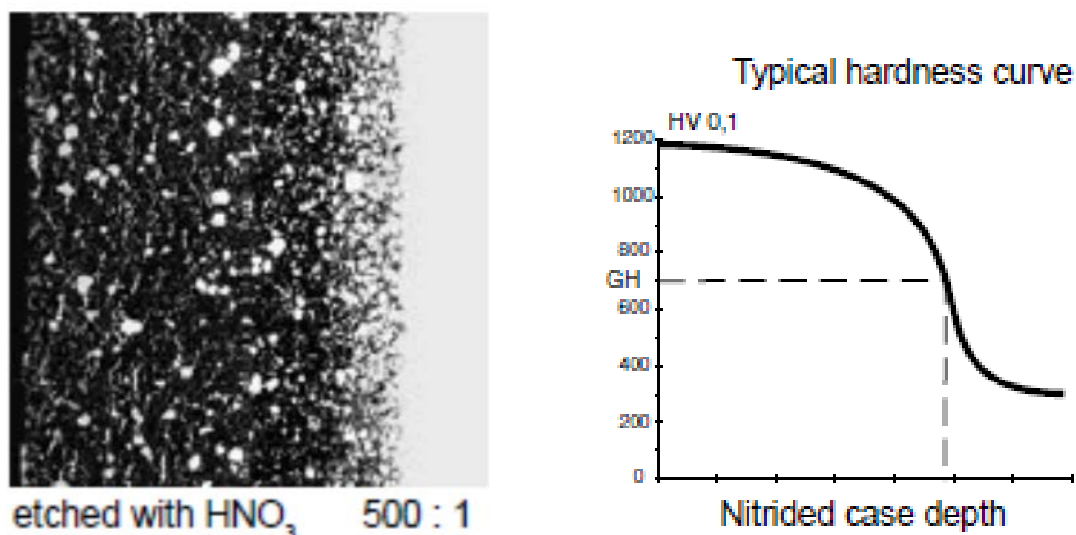


Figure 19: left: diffusion layer of nitrided chromium steel, right: typical hardness curve of nitrided material
Source: http://korihandbook.federalmogul.com/en/section_67.htm

Nitriding and nitrocarburizing are heat treatment processes during which one or more dopant elements diffuse into the surface layer of the metal substrate. In gas nitriding, the atmosphere contains an excess of the dopant. In the case of nitrocarburizing, the dopants are carbon and nitrogen, for nitriding it is only nitrogen. The dopant elements are introduced in the form of reactive chemical compounds. The nitrogen compound used is ammonia NH_3 . For nitrocarburizing, carbon monoxide CO or carbon dioxide CO_2 is added.

During case hardening, the parts are subjected to high temperatures. As a consequence the process temperatures limit the substrates and applications. For each piston ring base material to be nitrided or nitrocarburized, process parameters must be found so that the maximum acceptable temperature without loss of mechanical properties or distortion is not exceeded.

The case hardened area varies depending on time and temperature of the process. The longer the treatment and the higher the temperature, the deeper the dopant is introduced into the substrate. For piston rings, temperatures up to 600 °C are used, depending on the base material.

Nitriding/nitrocarburizing is mainly used for case hardening of chromium steel. Occasionally, it is also carried out on cast iron piston rings. In such instances the nitrided case is characterized by the formation of iron nitrides. The diffusion layer has the effect of improving ring performance compared to the uncoated cast iron material, especially in the case of heat-treated cast irons, due to the hardness increase.

A non-exhaustive overview of general information of substances used within this alternative and the risk to human health and the environment caused by these substances, is provided in Appendix 1.1.1.

6.1.2 Technical feasibility

General assessment: Nitriding/nitrocarburizing is used for specific piston ring applications where requirements concerning wear, scuff resistance and friction are relatively low. Typical applications are the piston rings of the first and third groove in LVP engines as used in passenger cars.

Nitriding is an application that is e.g. needed to prevent steel rings in steel piston grooves from wear defects. It is then used as axial wear resistance coating on the top and lower ring surface. It is whatsoever not a running surface coating. The tribological behaviour of a nitrided running surface is less beneficial than functional chrome plating.

Wear resistance: The properties of the hardened case strongly depend on the **base material**. Case hardening processes result in a structural change of the substrate, leading to increased hardness of the surface-near area with softer metal underneath. Hardness decreases with increasing depth from the substrate surface. The surface hardness of nitrided material exceeds that of a martensitic cast iron or steel and can increase **wear resistance** compared to uncoated material. Nitrided cast iron does not reach the same wear resistance as nitrided high-chromium steels, as iron nitrides do not improve wear resistance as much as chromium nitrides. This does not fulfil the requirements for compression rings in LVD and HD engines (ring 1 and 2). In order to achieve a sufficiently high wear resistance, the choice of base materials is limited to high-alloyed and therefore expensive chromium-alloyed materials. Functional chrome plating provides better wear resistance (**Figure 20**).

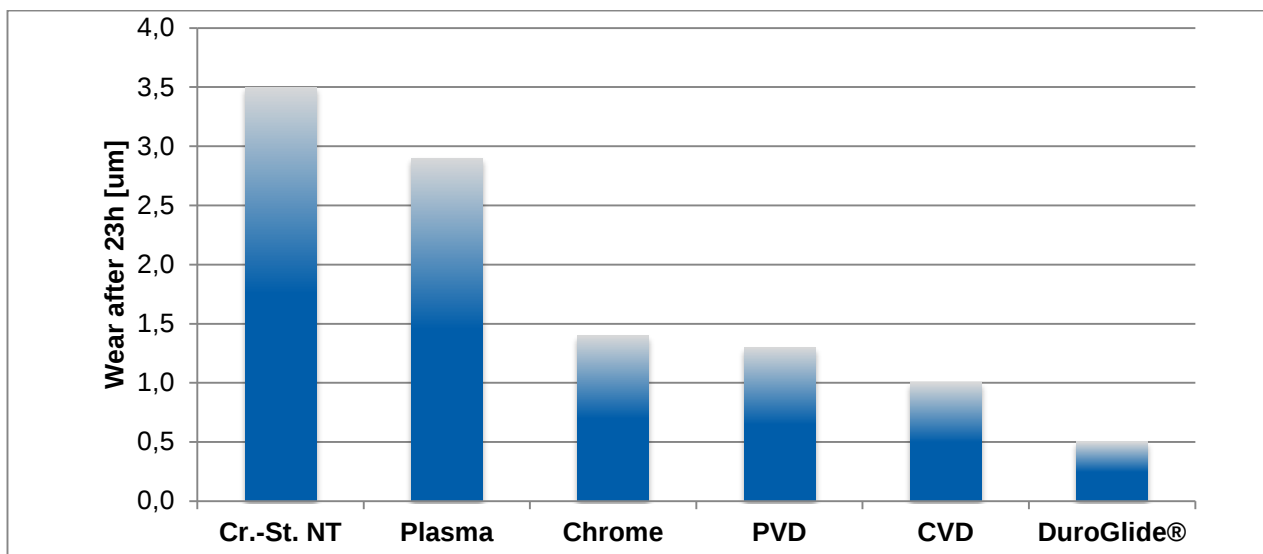


Figure 20: Wear resistance of several piston ring coatings in comparison. Cr.-St- NT = nitrided chromium steel. (Results obtained from Rig-Test).

Coefficient of friction: As the Rig-Test results in **Figure 21** depict, nitriding leads to a higher coefficient of friction compared to metallic chrome coatings. The high coefficient of friction leads to high abrasive wear for case hardened surfaces. At the same time the thickness of the case hardened surface (see below) is limited. The case hardened surface is removed by wear rather quickly, which is why the life-time expectations for the piston rings are not met for all types of piston rings.

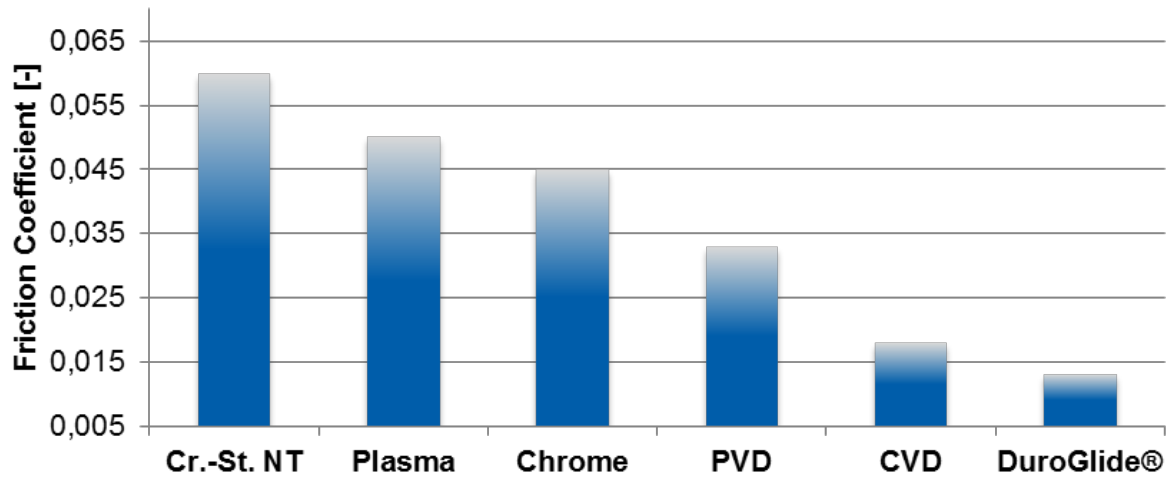


Figure 21: Friction coefficient of several piston ring coatings in comparison: Cr.-St- NT = nitrided chromium steel; (Results obtained from Rig-Test).

Scuff resistance: **Figure 22** shows that scuff behaviour of nitrided piston ring surfaces is inferior to functional chrome plated piston rings. Scuff resistance of nitrided piston rings is only sufficient for a few types of petrol engines. In contrast to functional chrome plating, it is insufficient for application in diesel engines and in high-stress petrol engines with specially coated cylinder liners. Therefore nitriding is technically no feasible alternative to functional chrome plating.

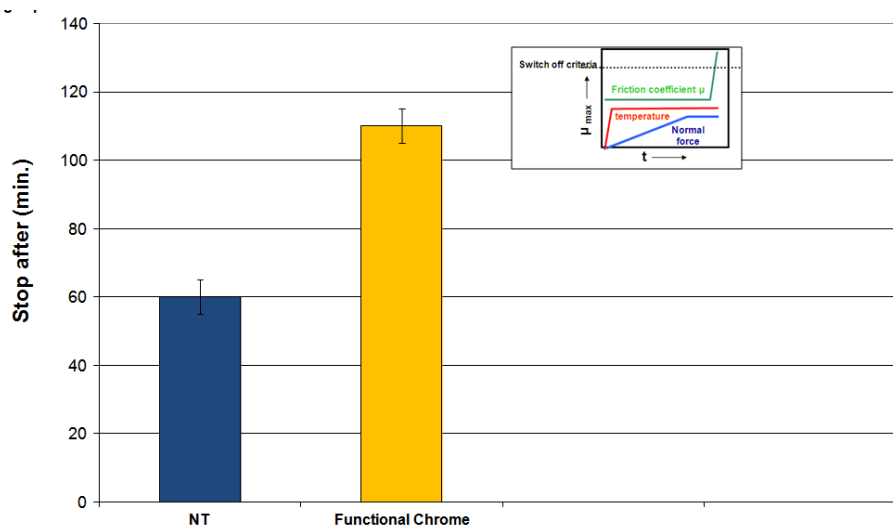


Figure 22: Scuff Rig-test: Nitrided piston ring surfaces compared to functional chrome plated piston rings. NT= nitrided

Hardness: The properties of the hardened case depend strongly on the substrate material. Therefore, for piston ring applications, mainly high-alloyed steels with a chromium content of 11 to 17 % are used. For these materials, nitriding creates chromium nitrides within the diffusion layer. This layer has a surface hardness greater than 900 HV 0.1. Towards the core of the substrate, the hardness decreases gradually. The thickness of the nitrided case is defined as the depth where the hardness is 700 HV 0.1, as defined in DIN 50190, part 3. Typically it is between 50 and 70 μm .

Machinability: Case hardened surfaces are in general quite brittle and tend to chipping. In addition, the case hardened surface loses its ductility. This does not allow the manufacture of sharp lower running edges where a perfectly intact coating is required. Sharp lower running edges are a special

geometry design feature that can be used for piston rings that are needed to reduce oil consumption. This property is usually required for oil control rings (3rd groove). In contrast to case hardening functional chrome plating allows the production of piston rings with sharp lower running edges. Sharp lower running edges are often applied in diesel engines as due to their better sealing properties, oil consumption and blow-by can be reduced. For such applications nitriding/nitrocarburizing is not an applicable alternative to functional chrome plating.

Thickness of the case hardened surface: Due to the tendency to chipping and the risk of ring fracture, thickness of case hardened surfaces is limited. For compression rings layers not exceeding 50 -70 µm are feasible, while functional chrome plating allows production of thicker coatings.

Corrosion resistance: Chromium-alloyed “stainless” steels used for piston rings exhibit a good resistance to **corrosion** in many acid media. If they are nitrided, this property is severely limited. Case hardening is not intended to provide corrosion protection. If protection of piston ring side faces is needed under corrosive influences, for example created by Exhaust Gas Recirculation (EGR), chromium coatings offer better corrosion resistance against nitric acid condensate than nitrided surfaces. This can be observed in countries where fuel quality is comparatively poor as poor fuel qualities are more corrosive. In such cases nitriding/nitrocarburizing does not provide a sufficient corrosion protection in contrast to functional chrome plating. Within the EU this is not an issue.

Geometry/edge design: As mentioned before, for case hardened surfaces the risk of chipping and ring fracture does not allow all kinds of ring geometries to be produced, while functional chrome plating allows processing of many different piston ring designs. Therefore case hardening is not a suitable alternative to replace functional chrome plating.

Side face protection: The nitrided case forms on the complete surface of the piston ring including the side faces. Therefore, side face protection is possible with this method. However, the layer properties are strongly dependent on the base material. Adequate side face protection is only achieved for high-chromium steels. This severely limits the choice of materials for piston rings that need side face protection.

Assessment overview for case hardening			
Wear resistance	Coefficient of friction	Scuff resistance	Hardness
			Depends on substrate and processes
Machinability	Corrosion Resistance	Geometry/ edge design	Side face protection

6.1.3 Economic feasibility

As the insufficient tribological properties of nitrided/nitrocarburized surfaces do not allow for a complete replacement of chromium trioxide functional chrome plating for piston ring applications, no quantitative analysis of economic feasibility was conducted. Due to the required high temperatures, case hardening is energy intensive compared to functional chrome plating.

6.1.4 Reduction of overall risk due to transition to the alternative

The substances and products used in the nitriding/nitrocarburization process were reviewed for comparison of the hazard profile. Based on the available information on the substances used within

this alternative (see Appendix 1.1.1), carbon monoxide is classified as Press. Gas, Flam. Gas 1, Acute Tox. 3, Repr. 1A, STOT RE 1. As such, transition from chromium trioxide – which is a non-threshold carcinogen – to one of the above mentioned alternatives would constitute a shift to less hazardous substances.

6.1.5 Availability

Case hardening (nitriding/nitrocarburizing) is a well-defined process that is commercially available (TURI, 2006), but its suitability as a running surface coating for piston rings is limited. It is not expected to become a one-to-one replacement for chromium trioxide in functional chrome plating in the future.

6.1.6 Conclusion on suitability and availability for alternative case hardening

Case hardening can fulfil the requirements for piston rings depending on the substrate and process for some applications.

However, nitriding/nitrocarburizing is not a replacement for chromium trioxide functional chrome plating for all applications. It cannot be used where high wear resistance and scuff resistance, long lifetime, low coefficients of friction or high corrosion resistance are needed. The dependency of the nitrided case structure on the base material limits the choice of base material to high-chromium steels, the brittleness limits the possible design features.

In summary, nitriding/nitrocarburizing processes are not a general alternative for functional chrome plating.

6.2 ALTERNATIVE 2: High velocity oxygen fuel spraying (HVOF)

6.2.1 Substance ID and properties

High velocity oxygen fuel spraying (HVOF) is a thermal spray process that can be used to apply running surface coatings onto piston rings. HVOF coatings offer the highest quality within thermal spray processes because of the high speed of the particles.

During the high velocity thermal spray process, coating powder is injected into a supersonic flame that accelerates the powder particles to high velocity. The heat of the flame melts these high-speed powder particles, which hit the substrate and flatten in pancake-shaped “splats”, see **Figure 23**. As they overlay each other, these splats form a coherent and low porosity coating (Legg K., 2003). The continuous flame HVOF process uses a gun with an internal combustion chamber where combustion fuels, for example kerosene, mixed with oxygen are fired continuously. These gases mixed with oxygen produce gas temperatures of about 1600°C when burned. The substrate is heated to app. 250°C.

The coating powder is injected axially into the flame where it heats and softens on its way to the substrate surface. The distance between the gun and the substrate has to be sufficient (15-30 cm) in order to heat the particles adequately before they hit the substrate (Legg K., 2003). The coating process is mostly conducted by a robot or other articulating arm equipped with the HVOF gun. The HVOF process is very fast with deposition rates of ca. 50 µm/min. The deposition of a 100 µm thick coating onto a cylinder (diameter 0.1 m, length 0.5 m) therefore generally takes less than 30 minutes, which is faster than for galvanic coatings.

In general, high velocity thermal spray processes offer a choice of possible starting powders, gases, types of equipment, coating materials and deposition conditions and are therefore very versatile. It is possible to spray most metals, alloys and some carbides. Most commonly, cermet coatings such as WC–Co, WC–CoCr and Cr_3C_2 –NiCr are applied via HVOF. Compositions in use for piston ring applications are typically made of a nickel-chromium matrix with tungsten carbide/chromium carbide (Cr_3C_2 –NiCr).

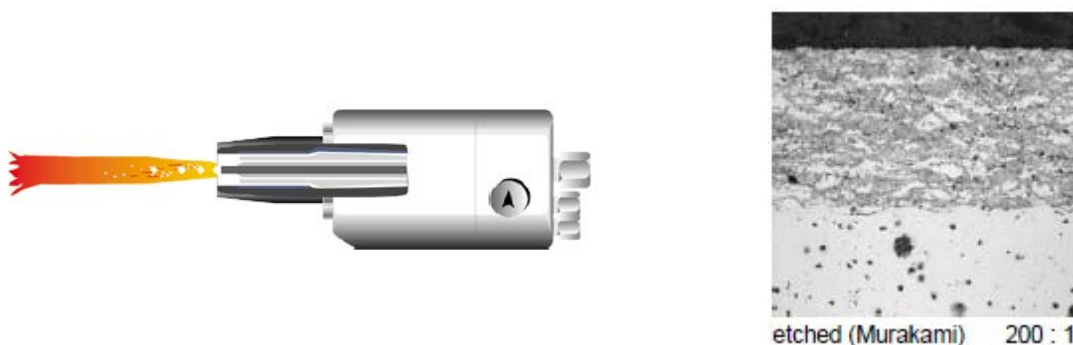


Figure 23: Left: HVOF Spray Gun; right: Cross section of a HVOF deposited coating.

Source: http://pcs.federalmogul.com/ProductLiterature/GOE_PistonRingBrochure_new9853c6bf-e3df-4f05-96df-c5d49c132a3c.pdf; right image: http://koriahandbook.federalmogul.com/en/section_67.htm

Due to overspray, the deposition efficiency is typically below 50 %. This means that only less than half of the powder used actually forms the coating. This is discussed in more detail in chapter 6.11.

In order to prevent heat build-up in any area either the gun or the substrate are moved over the respective counterpart. Additionally these thermal processes are equipped with cooling air-jets placed around the part to be coated. Cooling systems make it possible to coat heat sensitive substrates (e.g. aluminium and high strength steel).

The process generally takes place in a booth that provides an acoustic and dust enclosure to control the process noise that can reach noise levels of 130-140 dB (decibel). A non-exhaustive overview of general substances information used for chemical vapour deposition of HVOF coatings and the risk to human health and the environment caused by these substances, is provided within Appendix 1.1.2.

6.2.2 Technical feasibility

General assessment: The performance of the HVOF process clearly depends on the coating materials used. At Federal-Mogul, WC/ Cr_3C_2 –NiCr is used.

Wear resistance: When coatings containing a high amount of carbides like WC or Cr_3C_2 are applied via HVOF, the process results in very hard and wear-resistant coatings. From tribological testing it was shown that the wear resistance of HVOF-based coatings can be similar to CKS, but is worse than GDC. Generally, these coatings contain a high amount of ceramics (50 – 70 vol. % of carbides). As these materials are of limited adhesion to metallic matrices, breakages can occur, leading to decreased wear resistance for rings and liners. In contrast, the strength of matrix is superior in CKS and GDC in combination with less brittleness.

Coefficient of friction: The tribological behaviour of HVOF coatings on grey cast iron cylinder liners is clearly insufficient as the friction values are higher than every chromium application (**Figure 24**).

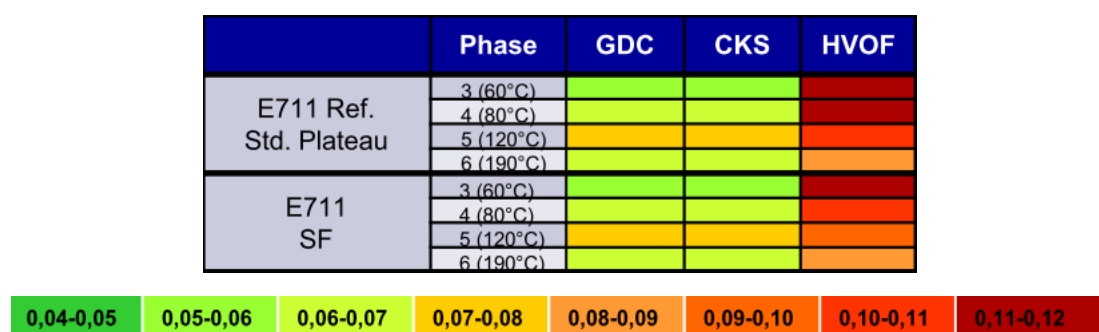


Figure 24: Coefficient of friction results from Rig test with legend below.

Liner Wear: The liner wear depends on how resisting the liner material is to the abrasive wear of the HVOF coated ring. By using HVOF coatings, one enforces the ring in terms of wear resistance improvement. Rig test results of a tribometric test in which a reciprocating ring sample runs against a cylinder liner segment under defined lubrication and load, showed that the specific wear on the cylinder liner side rises significantly. The very hard carbide coatings on ring side generate massive abrasive wear on the cylinder liner side (W- and Cr and Ti carbides are also needed in various production processes such as grinding, turning, etc.). Taking a look at the entire tribological system, it is obvious, that enforcing just one side leads to a weakening of the entire system by generating high clearance between the ring and the liner. Consequently, lubrication properties become insufficient and the reliability of the whole system is significantly reduced.

Hardness: The hardness of the final product can be controlled by the composition of the coating powder. For a piston ring coating, minimum requirements are between 850-1200 HV. Whilst metallic chrome coatings achieve between 800 - 1,200 HV, HVOF coatings can reach 1,500 HV.

Machinability: HVOF coating consist of rough surfaces that require, depending on the application, post treatment. This process step can be very expensive, because e.g. cost for tools are higher due to increased abrasion of tools and reduced ablation rate. Due to the specific process conditions, rings adhere to each other as they usually are piled on a mandrel to allow a high number of rings to be coated. Therefore, mandrel handling is necessary. Machinability of HVOF coatings is more demanding than post-processing of metallic chrome coatings.

Adhesion: Adhesion to the substrate was shown to be clearly insufficient compared to chrome coatings. Generally these coatings contain a high amount of ceramics (50 – 70 V% carbides). As these materials are of limited adhesion to metallic matrices, breakages can occur leading to decreased wear resistance for rings and liners.

Layer Thickness: The coating can be sprayed up to 500 µm thick directly to the designated location. The thickness is limited by residual stress of the coating that potentially lead to ring deformation. For automotive applications, the necessary coating thickness can be achieved.

Corrosion resistance: Dependent on the composition of the coating powder and porosity, the corrosion resistance can be varying to a certain extent. At Federal-Mogul, experience with WC/Cr₃C₂-NiCr demonstrated that the corrosion performance of these coatings is sufficient for the use in automotive applications.

Geometry of coated parts/Edge Design: HVOF as a line-of-sight process is limited in terms of coating complex shapes and inner surfaces. A minimum gun-to-substrate distance (stand-off) is required to achieve softening and acceleration to high velocity of the powder. However, by modification/rotation of the gun or table, it is possible to coat piston rings with higher dimensions (up to 980 mm). In principle, opening diameters of piston rings for automotive applications can be manufactured. HVOF

can be used for coating of compression rings only. The production of oil control rings, which require sharp edges, is very complicated and thus not practical with HVOF. As mentioned before, sharp edge designs are well feasible with functional chrome plating.

Coatings of inlayed rings can be produced. But the risk of deformation caused by blasting prior to coating and residual stress, which is a consequence of not fully melted powder particles, needs to be taken into account. Blasting before coating is necessary to allow a good adhesion of the material. The production of oil control rings is very complicated.

Side face protection: The use of HVOF coatings as a side face protection is hardly feasible. The coating would form in a non-uniform way on the side face and the running surface. This would mean that the running surface of every single ring would have to be protected during side face coating in order not to impair the running surface. Because of the roughness of the coated surface, the side faces would have to be extensively machined with a high likeliness of chipping off of the coating.

Assessment overview for HVOF				
Wear resistance	Coefficient of friction	Liner wear	Hardness	Machinability
Adhesion	Layer Thickness	Corrosion resistance	Geometry/Edge Design	Side face protection

6.2.3 Economic feasibility

Against the background of significant technical failure of HVOF, no quantitative analysis of economic feasibility was conducted. However, the cost for HVOF depends on numerous different factors and these are presented in a qualitative to semi-quantitative way below. The technology for high velocity processes and functional chrome plating differ fundamentally in the equipment and peripherals. The implementation of high velocity processes requires complex machines and infrastructure equipment.

Energy and material expenditure are enormous. With a consumption of 25 L/h kerosene, 900 l/min oxygen and 100g/min powder, a maximum application performance of 6 kg can be reached. Carbide-powder materials are rather costly. Application efficiency is at about 30 – 40 % (max. 50 %). Therefore, the coating material costs are by far the biggest driver for increasing costs. An R&D project at F-M showed that the costs for production of HVOF coated piston rings were considerably higher than for CKS without improving ring function.

Functional chrome plating processes are mostly automated and are well known since they have been applied for decades. HVOF coatings are a completely different technology and require workers with adequate new skills who follow with constant attention and careful control the proper process definitions in order to achieve a coating of equal quality. In addition, the process has to take place in booths due to the noise and dust formation and requires complex and cost intensive peripheral equipment as well as additional space requirements on the premises.

6.2.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of WC/Cr₃C₂-NiCr, kerosene and oxygen gas (see Appendix 1.1.2) were reviewed for comparison of the hazard profile. The metal powders (Ni, Cr) pose an additional health risk. Aspiration and noise-

protection cabin are required. The powder cannot be recycled. Overspray powder is therefore hazardous waste.

As mentioned above, various different powder materials are used for high velocity processes. As an example, the hazard profile from an often-used coating material is illustrated. According to suppliers' safety data sheet (SDS), the following hazard statements are given for WC/ Cr₃C₂-NiCr: Eye Irrit. 2, Skin Sen. 1, Carc. 2, STOT RE 1. As such, transition from chromium trioxide – which is a non-threshold carcinogen – to WC/ Cr₃C₂-NiCr would only to a limited extend constitute a shift to less hazardous substances.

6.2.5 Availability

In general, HVOF processes are commercially fully developed. Equipment and powders can be obtained commercially from a number of vendors. At Federal-Mogul, this process is industrialized and used for specific LBE but not for automotive applications.

6.2.6 Conclusion on suitability and availability for alternative HVOF

These processes do not perform technically equivalent to chromium trioxide-based products and are therefore not a general alternative. Some HVOF coatings are currently used for a limited number of specific applications. The process inherent application of the metal powder via a gun barrel (line of sight process) excludes complex geometries and internal parts from being HVOF coated. Apart from the geometrical restrictions, the alternative shows technical failure in very important sector specific performance parameters such as adhesion to the substrate material.

In conclusion, these systems are technically not equivalent to chromium trioxide-based products, have strong economic disadvantages and are therefore not a general alternative.

6.3 ALTERNATIVE 3: Physical vapour deposition (PVD) – CrN-based coatings

6.3.1 Substance ID and properties

Physical Vapour Deposition technology (PVD) for piston ring running surfaces is a method of depositing hard coatings reactively from the vapour phase in a high-vacuum process. Coating compositions in use for piston rings are based on chromium nitride (CrN), chromium oxynitride (CrON) or multi-layered coatings of chromium nitride and aluminium titanium nitride (CrN/AlTiN). As the coating compositions produced by PVD in use for piston rings are based on chromium nitride (CrN), in this document the term PVD is used to refer to chromium nitride based PVD coatings only. **Figure 25** below depicts a PVD production unit.

Recently, a process was developed at Federal-Mogul to deposit hydrogen-free diamond-like carbon coatings (DLC) by a physical vapour deposition process (hereafter also referred to as *thick DLC*) (Kennedy et al, 2014). This alternative will be assessed in chapter 6.22.

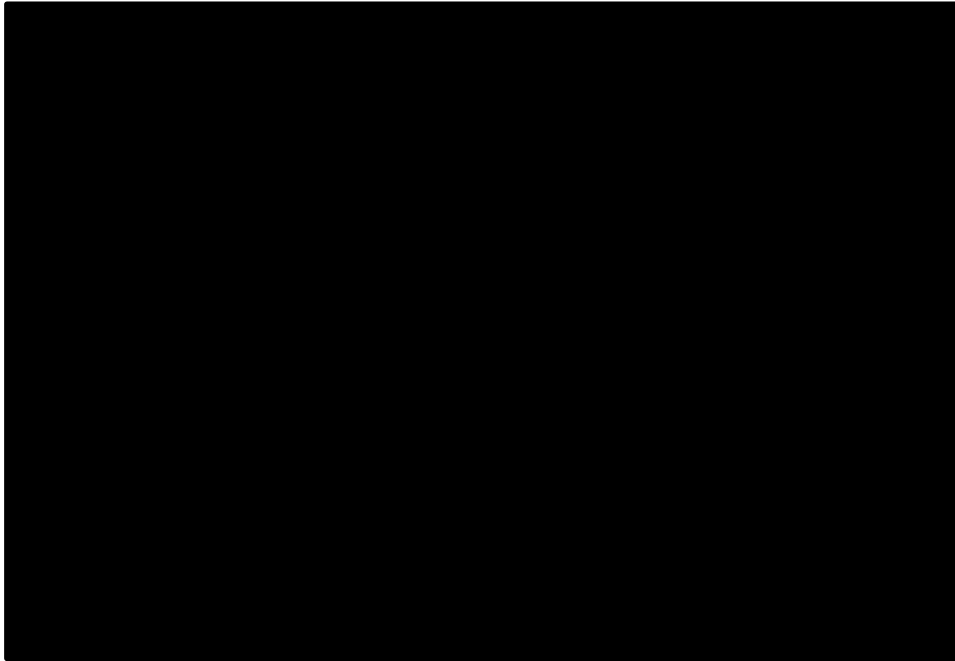


Figure 25:

The PVD coating process involves vaporizing and ionizing a metal from a target by means of an arc or an inert gas ion bombardment. The metal ions are accelerated to the surface of the component, discharged and deposited. In the reactive process the metal atoms react with the reactive gas atoms. This causes dense coatings to form on the surface of the component.

The principle of PVD coating with CrN is shown in **Figure 26**.

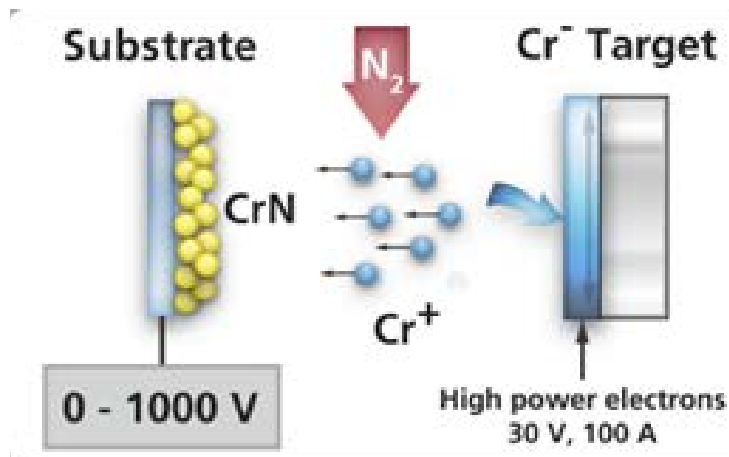


Figure 26: Principle of the PVD coating technique

Source: http://pcs.federalmogul.com/ProductLiterature/GOE_PistonRingBrochure_new9853c6bf-e3df-4f05-96df-c5d49c132a3c.pdf

The conditions for PVD coatings are process specific and dependent on the substrate and applied coating. The method is limited by the maximum temperature the substrate can support without loss of mechanical properties or deformation. PVD coating temperatures suitable for piston ring materials must be below 600 °C for steel material and below 450° C for cast iron. The properties of PVD coatings for piston rings depend on their structure. The most common material in use, chromium

nitride CrN, is an interstitial compound where nitrogen atoms occupy the octahedral holes in the chromium lattice.

The coating process is complex and highly sensitive to contaminants (e.g. water or residues from cooling fluids from machining) on the surface to be coated. A substrate surface that is not clean on an atomic level will severely affect coating adhesion on the substrate and can be a cause for increased coating porosity.

A non-exhaustive overview of general information and the identity of relevant substances used within this alternative and the risk to human health and the environment is provided in Appendix 1.1.3.

6.3.2 Technical feasibility

PVD coatings are currently in use in a number of piston ring applications. There are aspects that make PVD coatings suitable for LVP, LVD and HD applications. However, they are unlikely to replace chromium trioxide functional chrome coatings completely within the next 15 years due to several limitations. It is important to note that the suitability of a piston ring coating needs to be looked at as part of the system piston rings – cylinder liner.

The conditions for PVD coatings are process specific and dependent on the substrate and the applied coating. PVD technology has just been established there within the past 10 years.

Wear resistance: Both pure CrN and CrN-based coatings show a good wear resistance. As **Figure 27** depicts, the wear resistance of CrN-based PVD coatings is on the same level as that of metallic chromium trioxide coatings like.

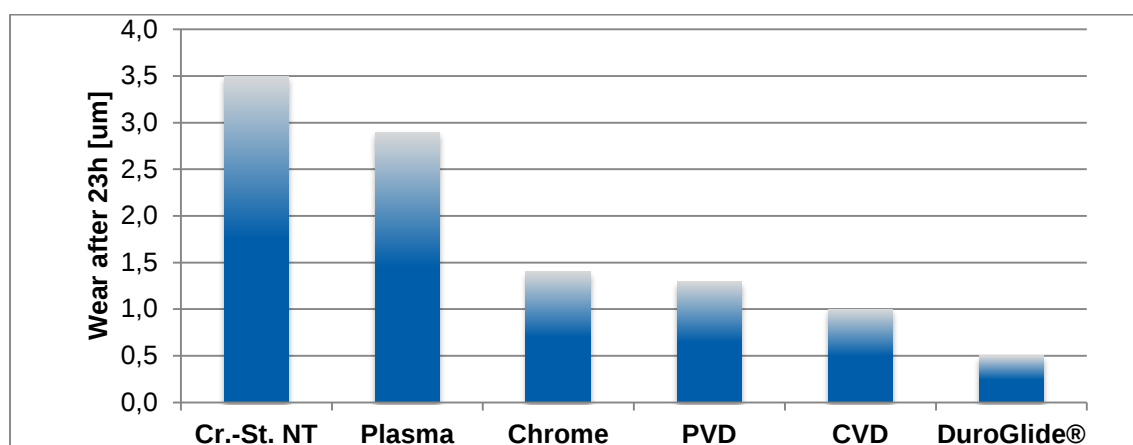


Figure 27: Wear resistance of several types of piston ring coatings in comparison (Results obtained from Rig-Test).

However, for HD applications, PVD coatings do not provide satisfying results in terms of wear resistance. Disadvantageous shaping of the rings due to the limited layer thickness results in coating properties that induce thermal expansion of the ring material which in turn increases wear rates. In contrast, this is not an issue for functional chrome plating, as these coatings are of higher thickness and in turn can better compensate shaping issues.

Coefficient of friction: For CrN-based PVD coatings, a reduced coefficient of friction of about 20 % compared to metallic chrome coatings was demonstrated in the Rig-Test as illustrated in **Figure 28**.

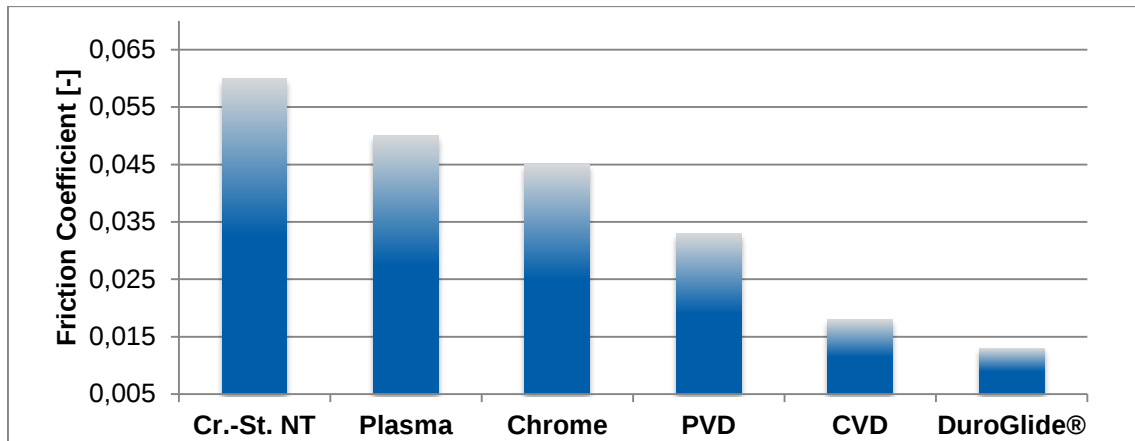


Figure 28: Friction coefficient of several piston ring coatings in comparison (Results obtained from Rig-Test)

Scuff resistance: Both pure CrN and CrN-based coatings show a scuff resistance that is above the scuff resistance of pure chrome or reinforced chrome coatings with embedded aluminium oxide or diamond.

Hardness: The hardness of PVD coatings depends on the coating material and the process parameters. For CrN coatings, typical values range from 800 to 1400 HV 0.1, for CrON from 1500 to 2200 HV 0.1. The key functional requirement for automotive application as obtained by functional chrome plating is 850-1,200 HV. Thus hardness of PVD coatings is sufficient for piston rings for automotive applications.

Machinability: The need of a vacuum chamber limits the size and number of parts that can be coated. As the size for vacuum chambers is limited for physical reasons, batch size decreases considerably with increasing size of the plated parts. In addition, machining of the piston rings before and after coating is more critical than for chrome-plated rings. In order to avoid rough surfaces, additional polishing steps are necessary.

Layer thickness: CrN PVD coatings are brittle and tend to chipping. Dependent on coating material and process parameters, they typically possess high residual compressive stress. The higher the coating thickness, the more critical is the stress level. It can lead to delaminating of the coating, cracking, or even deformation of the coated piston ring. The inner stress level limits the maximum coating thickness to 50 µm for CrN or similar coatings. Chromium trioxide functional chrome coatings are not limited in the coating thickness and possess a similar wear rate as CrN-based coatings. Additionally, with increasing coating thickness, the deposits become rougher. Because of their high hardness and brittleness, this complicates machining.

A typical coating thickness for LVD and HD applications is 30 µm, for the application in piston rings for diesel engines the layer thickness that can be achieved by PVD coating is usually appropriate. For applications where a very long lifetime under severe wear conditions is needed, the achievable coating thicknesses may not be sufficient.

Corrosion resistance: The above-mentioned PVD coatings are reported to be essentially inert and do not corrode. However, they do not provide as much corrosion resistance as do thicker chromium coatings. Especially once the coating is damaged, the corrosion protection provided by the layer degrades compared to metallic chrome coatings. The resistance of the above-mentioned PVD coating materials against chemical attack and corrosion is high. In practical use it is limited by pinholes going through to the base material or cracking under mechanical stress. If the coating is damaged, corrosion

of the substrate is possible. For most piston ring applications, this is not the decisive factor when assessing the technical feasibility of PVD coatings.

Geometry/edge design: Sharp lower running edges are a valuable design tool for oil consumption rings. While functional chrome plating is highly applicable for such kinds of ring designs, this cannot be achieved with PVD coatings due to their tendency to chipping. The high residual compressive stress in the coatings can adversely affect the shape of the piston ring and thus deteriorate ring function. Chrome-plated piston rings are coated in a state similar to the assembled state in the engine. Therefore the coating will not disturb the ring shape. The inner stress of PVD coatings limits their use on cast iron even more than for steel materials, thereby making steel a preferred base material. This limits freedom of ring design and increases cost for base material.

Side face protection: The use of PVD coatings as a side face protection is hardly feasible. The coating would form in a non-uniform way on any surface exposed during the process. This would mean that the running surface of every single ring would have to be protected during side face coating in order not to impair the running surface and make such a process highly inefficient.

Material Compatibility: the use of PVD on steel materials is state of the art. Change from functional Chrome/CKS/GDC to PVD on cast iron is done in single cases but would need more experience and development for large scale series production. To take PVD on cast iron into account, the major challenges will be a robust solution to cover the critical PVD layer bonding on soft cast iron material.

PVD does not yet meet the goals of modern combustion automotive engines. Its lack of capability to deal with requirements, such as directly coated engine blocks or extreme “dry” environment due to drastically reduced lubricating oil consumption, significantly reduces possibilities to introduce PVD coated rings to series applications.

Assessment overview for PVD based alternative				
Wear resistance	Coefficient of friction	Scuff resistance	Hardness	Machinability
Layer thickness	Corrosion resistance	Geometry/edge design	Side face protection	Material compatibility (cast iron / steel)

6.3.3 Economic feasibility

The technology for PVD processes and functional chrome plating differ fundamentally in the equipment and peripherals. The implementation of PVD requires complex machines and infrastructure equipment. Hypothetically, in order to supply the market with the required amount of piston rings, a total of ■ coating lines and ■ machines for pre- and post-treatment would need to be installed at F-M’s facilities in Burscheid, Dresden and Garennes-sur-Eure. As stated in the SEA the costs for just the equipment are estimated to account for ■. For further information the reader is referred to the SEA.

With the application of new technologies like PVD the production costs considerably increase compared to functional chrome plating. The increase in costs can be explained by the significantly less efficient production of PVD compared to functional chrome coatings like CKS/GDC. Mainly responsible for the significantly reduced process efficiency is the slow growth rate of the layer. While with functional chrome plating (GDC/CKS) layer growth rates of 63 µm/h are state of the art, for

PVD the deposition rates are 15 times lower. Typically, coating of one batch of piston rings takes at least one working shift of 8 hours. This makes the process more expensive for smaller batch sizes, i. e. larger dimensions of the parts. Additionally, in combination with the high costs of PVD equipment, the coating costs increase with increasing coating thickness and part size.

Moreover, additional manufacturing steps are necessary for the production of piston rings with PVD coatings. The additional steps are extensive surface polishing and grinding processes as well as edge treatments that have to be accomplished in separate steps for individual piston rings. At last, quality control has to be conducted with increased effort.

The consumption of electrical energy for the generation of the high-vacuum and the evaporation of the coating material is very high compared to the energy consumption of electrodeposition processes like chromium trioxide functional chromium plating.

Due to these enormous investments and costs related to switching to PVD is not considered an economically feasible alternative for functional chrome plating for piston rings for automotive applications at F-M.

6.3.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances 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 1.1.3), the dupplier's SDS classifies aluminium titanium nitride as causing metallic taste, nausea, tightness of chest, fever, irritation of eyes, nose, throat and skin, loss of consciousness/death due to welding gases or lack of oxygen. However, transition from chromium trioxide – which is a non-threshold carcinogen – to one of these substances would constitute a shift to less hazardous substances.

6.3.5 Availability

PVD is a well-known technology that is used for piston ring coatings within and outside the EU. PVD process equipment is commercially available. At Federal-Mogul, this process is available and industrialized for specific applications. However, as stated in the SEA, for piston ring coatings special PVD-equipment is necessary in order to apply coating thicknesses up to 10 times higher than state of the art. Since only a small number of suppliers provides this specialised equipment not more [REDACTED] machines can be installed per year. Thus [REDACTED] would be necessary to install the [REDACTED] coating lines needed to serve the market. Additionally, the process is only feasible for specific applications as stated above and significant technical and economic issues would need to be overcome to develop PVD to be a general functional chrome plating alternative for piston rings in automotive applications.

6.3.6 Conclusion on suitability and availability for alternative PVD

PVD was assessed with regard to existing production-scale methods and special requirements for piston rings. For several applications coatings applied by PVD already perform technically equivalent to chromium trioxide derived products. The design restrictions and insufficient performance in side face protection prohibit their use as a general alternative.

Furthermore, the high investment cost combined with lower productivity and much longer process times lead to high plating costs, especially for bigger parts. In order to coat the complete number of piston rings that today possess chromium trioxide-derived functional chrome coatings, enormous

investments would be needed. Due to the specialised equipment required in this case, the alternative could also not be implemented on short hand.

Ultimately, the cost of PVD coatings for piston rings is significantly higher than for functionally chrome plated piston rings, while the ring function is not improved. Therefore, the interest of the market to replace chrome-based coatings with PVD coatings is low.

6.4 ALTERNATIVE 4: Hydrogen-free DLC coatings (thick DLC)

6.4.1 Substance ID and properties

Physical Vapour Deposition technology (PVD) for the production of chromium nitride based coatings is discussed in chapter 6.16. Recently, a process was developed at Federal-Mogul to deposit hydrogen-free diamond-like carbon coatings (DLC) with PVD technology (DuroGlide[®], hereafter referred to as thick DLC) for piston ring applications. As this coating is fundamentally different from previous PVD coatings, it is discussed as a separate alternative. A non-exhaustive overview of general information and the identity of relevant substances used within this alternative and the risk to human health and the environment is provided in Appendix 1.1.4.

6.4.2 Technical Feasibility

Wear resistance: As **Figure 29** depicts, thick DLC coatings show higher wear resistance compared to chrome-based coatings.

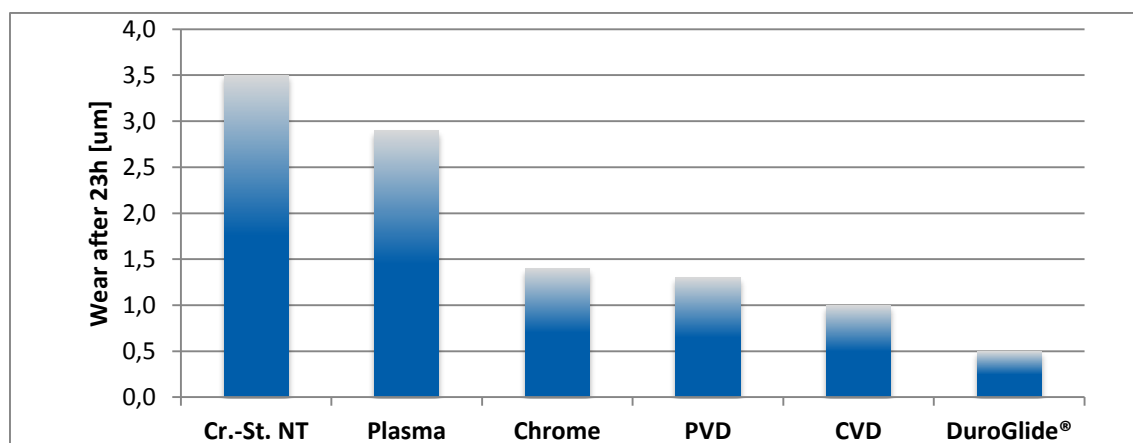


Figure 29: Wear resistance of several types of piston ring coatings in comparison (Results obtained from Rig-Test).

Coefficient of friction: Thick DLC coatings provide a coefficient of friction which is less than half as high as the friction coefficient of chromium trioxide functional chrome-based coatings or PVD chromium nitride coatings (**Figure 30**).

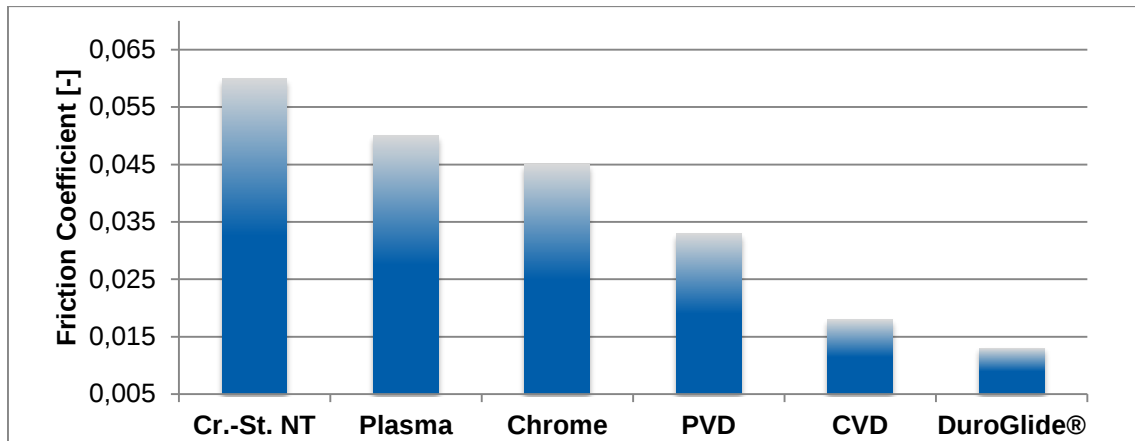


Figure 30: Friction coefficient of several piston ring coatings in comparison (Results obtained from Rig-Test)

Scuff resistance: Thick DLC coatings show a scuff resistance that is above the scuff resistance of pure chrome coatings.

Hardness: Thick DLC coatings can possess a hardness of up to 5000 HV 0.2. The key functional requirement for automotive application as obtained by functional chrome plating is 850-1,200 HV. Thus hardness of thick DLC coatings is sufficient for piston rings for automotive applications.

Machinability: The need of a vacuum chamber limits the size and number of parts that can be coated. As the size for vacuum chambers is limited for physical reasons, batch size decreases considerably with increasing size of the plated parts.

Layer thickness: DLC coatings are brittle and tend to chipping. Dependent on coating material and process parameters, they typically possess high residual compressive stress. The higher the coating thickness, the more critical is the stress level. It can lead to delaminating of the coating, cracking, or even deformation of the coated piston ring. The maximum obtainable coating thickness, limited by the inner stress levels, for F-M's hydrogen-free DLC coating process is 25 µm. Therefore, in applications where a higher wear reserve is needed, the alternative is not feasible. Chromium trioxide functional chrome coatings are not limited in the coating thickness, granting the extra wear reserve. Additionally, with increasing coating thickness, DLC deposits become rougher. Because of their high hardness and brittleness, this complicates machining.

Corrosion resistance: The thick DLC coatings are reported to be essentially inert and do not corrode. However, they do not provide as much corrosion resistance as do thicker chromium coatings. Especially once the coating is damaged, the corrosion protection provided by the layer degrades compared to metallic chrome coatings. The resistance of the thick DLC coating material against chemical attack and corrosion is high. In practical use it is limited by pinholes going through to the base material or cracking under mechanical stress. If the coating is damaged, corrosion of the substrate is possible. For most piston ring applications, this is not the decisive factor when assessing the technical feasibility of thick DLC coatings.

Geometry and edge design: Sharp lower running edges are a valuable design tool for oil consumption rings. While functional chrome plating is highly applicable for such kinds of ring designs, this cannot be achieved with thick DLC coatings due to their tendency to chipping. The high residual compressive stress in the coatings can adversely affect the shape of the piston ring and thus deteriorate ring function. Chrome-plated piston rings are coated in a state similar to the assembled state in the engine. Therefore the coating will not disturb the ring shape.

Side Face Protection: The use of thick DLC coatings as a side face protection is hardly feasible. The coating would form in a non-uniform way on any surface exposed during the process. This would mean that the running surface of every single ring would have to be protected during side face coating in order not to impair the running surface and make such a process highly inefficient.

Assessment overview for thick DLC				
Wear resistance	Coefficient of friction	Scuff resistance	Hardness	Machinability
Layer thickness	Corrosion resistance	Geometry/ edge design	Side face protection	

6.4.3 Economic feasibility

The technology for the thick DLC processes and functional chrome plating differ fundamentally in the equipment and peripherals. Therefore the baths for functional chrome plating would have to be replaced completely by facilities for thick DLC. The implementation of thick DLC requires complex machines and infrastructure equipment. As stated in the SEA, about ■■■ coating lines and ■■■ machines for post- and pre-treatment would be needed on the three locations run by F-M in Burscheid, Dresden and Garennes-sur-Eure in order to be able to supply the market with the required numbers of piston rings. The installation of production equipment for F-M's hydrogen-free DLC technology alone is estimated to cost ■■■ in total. Further associated costs like new land or costs for the massively enhanced power supply are not included in this figure. For further information the reader is referred to the SEA.

With the application of new technologies like the hydrogen-free thick DLC coating the production costs considerably increase compared to functional chrome plating. The increase in costs can be explained by the significantly less efficient production of the hydrogen-free thick DLC coating compared to functional chrome coatings like CKS/GDC. Mainly responsible for the significantly reduced process efficiency is the slow growth rate of the layer. While with functional chrome plating layer growth rates of 63 µm/h are stand of the art, for thick DLC the rates are even more than 50 times lower.

Moreover, additional manufacturing steps are necessary for the production of piston rings with thick DLC coatings. The additional steps comprise extensive surface polishing and grinding processes as well as edge treatments that have to be accomplished in separate steps for individual piston rings. At last, quality control has to be conducted with increased effort.

Until now, F-M invested ■■■ into the development of its innovative hydrogen-free DLC coating technology. The costs include labour costs, investment and the costs for material (piston rings), internal validation and administration. The costs do not include development costs on the customers' side.

To sum it up, even though F-M is about to implement the thick DLC process for special applications, the thick DLC process is not regarded as an economically feasible alternative to replace functional chrome plating of piston rings at F-M.

6.4.4 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 (carbon and chromium) were reviewed for comparison of the hazard profile. Chromium and Carbon are both rated “not classified” by most notifiers. Carbon is further classified as Eye Irrit. 2 and STOT SE 3 by 748 notifiers. Chromium is classified Skin Sens.1 and Resp. Sens. 1 by 362 notifiers. Based on the available information on the substances used within this alternative (refer to Appendix 1.1.4) a transition from chromium trioxide – which is a non-threshold carcinogen – to one of these substances would constitute a shift to less hazardous substances.

6.4.5 Availability

The thick DLC process as invented by F-M is a new technology. Standard PVD process equipment is commercially available. However, at Federal-Mogul, the process is only feasible for specific automotive applications and significant technical and economic issues would need to be overcome to develop this to a general functional chrome plating alternative for piston rings. But for DLC specialised equipment is required. As stated in the SEA, due to the limited production capacity of the only DLC equipment supplier, the number of machines necessary for the implementation of the hydrogen-free DLC process cannot be produced in due time. For further information the reader is referred to the SEA.

6.4.6 Conclusion on suitability and availability of alternative hydrogen-free DLC coatings (thick DLC)

Despite its otherwise excellent technical properties the thin DLC process is not a technically feasible alternative to functional chrome plating in some applications such as piston rings with sharp edge design. Another decisive in this context is that the installation of production equipment is estimated to cost [REDACTED] in total. Moreover the theoretically necessary number of equipment is not available on the market. Therefore, thick DLC coatings are not regarded as an option to replace functional chrome plating for piston rings.

6.5 ALTERNATIVE 5: Chemical vapour deposition (CVD) – thin DLC coatings

6.5.1 Substance ID and properties

CVD as well as plasma-assisted chemical vapour deposition (PA-CVD) are assessed together as an alternative as they basically refer to the same process but with different process conditions (TURI, 2006 and RPA, 2005).

At Federal-Mogul, **hydrogen-containing (WCH/aCH) diamond-like carbon (DLC)** coatings are produced with a combination of PVD and PA-CVD processes. Therefore, only PA-CVD type of coatings and method is assessed in detail. Other CVD processes are not expected to possess advantages over existing PVD methods for piston ring applications. Due to the maximum achievable coating thickness of 8 µm, these coatings will be referred to as “**thin DLC**”.

CVD processes are operated in vacuum chambers. In the process, reactant gases, normally mixed with inert gases, enter the reaction chamber at room temperature. These so-called precursors are brought into the deposition area in the gas phase. They contain the desired coating materials such as metal halides, metal carbonyls, hydrides or organometallic compounds. Possible coating materials are e.g. titanium carbide, titanium nitride, titanium carbon nitride, silicon carbide, titanium boride, aluminium oxide or diamond-like carbon.

After being absorbed onto the surface of the substrate, the reactants are decomposed and react with the substrate to form the coating. The energy needed for decomposition of the precursors can either be supplied by heating the process gas or substrate, or in PA-CVD, by a plasma. The advantage of plasma-assisted CVD is that it is possible to only heat the surface region where the reaction occurs while the core of the component is maintained at a comparatively lower temperature. The process temperature for the production of thin DLC coatings by PA-CVD is below 200° C.

A schematic overview of the CVD process is presented in **Figure 31** below.

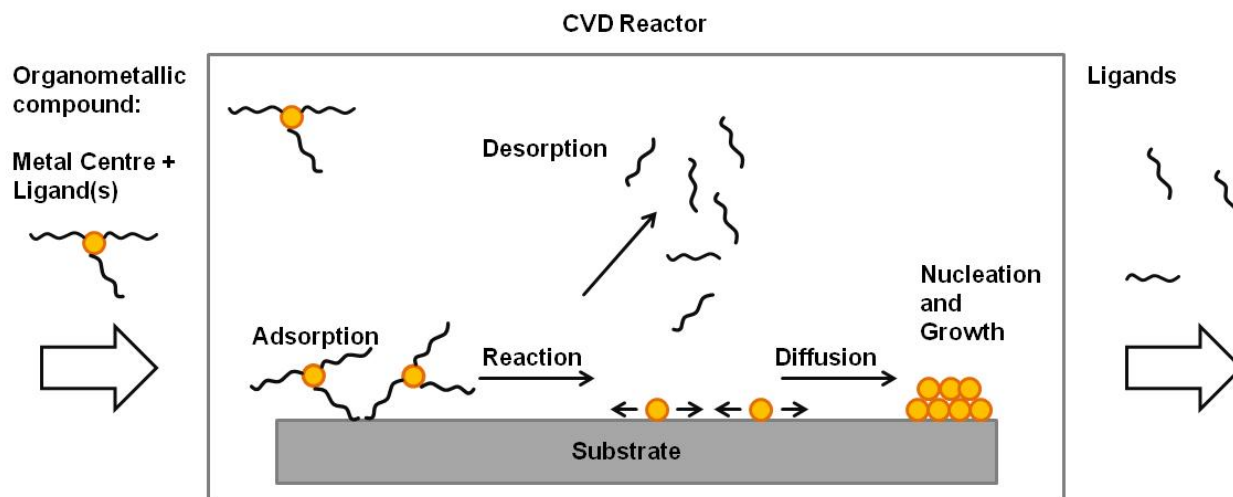


Figure 31: Schematic of chemical vapour deposition.

Substances used for thin DLC are acetylene and tungsten. A non-exhaustive overview of general substances information used for chemical vapour deposition of thin DLC coatings and the risk to human health and the environment caused by these substances, is provided within Appendix 1.1.5.

6.5.2 Technical feasibility

Properties of CVD coatings depend on the coating material and the process parameters. Thin DLC coatings from PA-CVD have an amorphous structure and contain roughly 30 % of sp^3 ("diamond") type bonds. DLC coatings are mainly used for piston rings in LVP engines with cylinder running surfaces made of high silicon aluminium materials. The thin DLC coatings contain hydrogen and are not suitable as a lifetime running surface coating for piston rings.

Wear Resistance: The wear resistance of thin DLC coatings is not significantly higher than for high-performance diamond-chromium coatings like GDC. Thin DLC-coatings are used as running-in surface only. Therefore thin DLC coatings are no suitable alternative to functional chrome plating of piston rings (**Figure 32**).

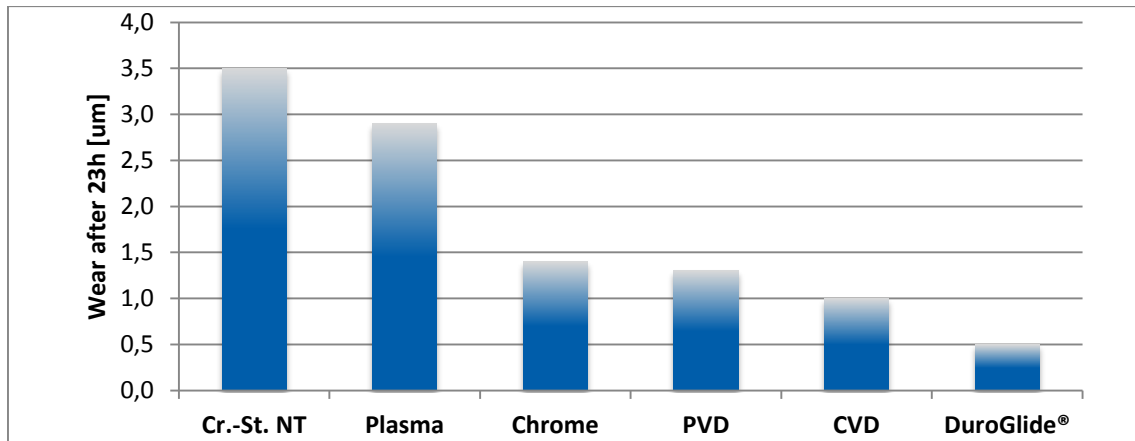


Figure 32: Wear resistance of several types of piston ring coatings in comparison (Results obtained from Rig-Test).

Coefficient of friction: Thin DLC coatings are known for their very low coefficient of friction (**Figure 33**). Their friction performance is sufficient for automotive applications.

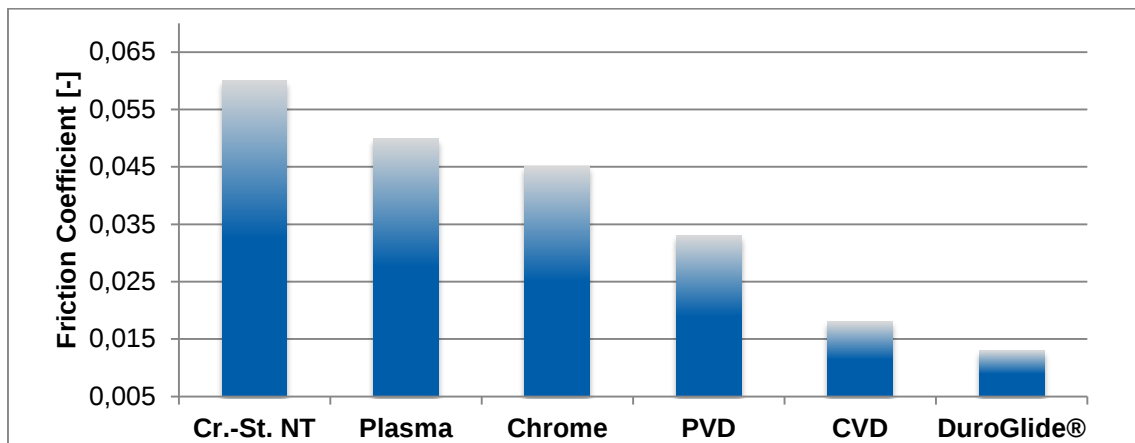


Figure 33: Friction coefficient of several piston ring coatings in comparison (Results obtained from Rig-Test)

Scuff Resistance: The scuff resistance of thin DLC coatings is higher than for metallic chromium coatings.

Hardness: Due to their structure, thin DLC coatings possess a very high hardness of up to several thousand HV. Hardness is an important key functionality of a metallic chrome coating. The minimum requirement for piston rings of 850-1,200 HV is fulfilled.

Machinability: Machining of thin DLC coatings is more complicated than for chromium trioxide functional chrome coatings. With increasing coating thickness, the surface becomes rougher and needs to be smoothed. However, mechanical post-processing is not practicable for thin layers. Due to the high hardness special machinery and processes are needed. The brittleness can result in chipping; therefore no sharp edge designs are possible. The need of a vacuum chamber additionally limits the size and number of parts that can be coated. As the size for vacuum chambers is limited for physical reasons, batch size decreases considerable with increasing size of the plated parts.

Coating Adhesion: The adhesion of thin DLC coatings to the substrate is generally weaker than for electrodeposited coatings such as chromium trioxide functional chrome coatings. It is strongly dependent on the cleanness of the substrate and the process parameters.

Layer Thickness: The maximum layer thickness that can be obtained for thin DLC coatings by PA-CVD processes is 8 µm. It is limited by both the slow deposition rate and the internal stress that causes deformation and delaminating of the coating. Although the specific wear resistance of the coating is higher than for chrome coatings, this limited layer thickness does not allow a reliable function of the engine over the expected service lifetime in conditions where higher wear can be assumed. Therefore, thin DLC coatings from a PA-CVD process can only be used for applications where little wear is expected (LVP) or as an additional coating on top of a case hardened surface. For most applications, especially the diesel segment, the layer thickness is not sufficient to allow reliable function over the expected service lifetime of the piston rings.

Corrosion resistance: Thin DLC coatings are chemically inert towards acid media. As they are electrically conductive, they behave much nobler than typical base materials. They can only provide protection of the base material as long as no porosities or other coating defects reaching the base material are present.

Geometry/Edge Design: In contrast to functional chrome plating geometries like sharp edge design are not feasible with PA-CVD.

Side Face Protection: The use of CVD coatings as a side face protection is hardly feasible. The coating would form in a non-uniform way on any surface exposed during the process. This would mean that the running surface of every single ring would have to be protected during side face coating in order not to impair the running surface and make such a process highly inefficient.

Assessment overview for thin DLC coatings from PA-CVD Process				
Wear resistance	Coefficient of friction	Scuff resistance	Hardness	Machinability
Adhesion	Layer Thickness	Corrosion resistance	Geometry/Edge Design	Side face protection

6.5.3 Economic feasibility

Against the background of technical failure of CVD, no quantitative analysis of economic feasibility was conducted. However, the cost for CVD depends on numerous different factors and these are presented in a qualitative to semi-quantitative way below.

CVD processes include relatively high costs because it is a complex technology that requires a vacuum chamber. The costs for the equipment are indicated to be more than one million US dollars for the coating system, with additional costs for pre- and post-treatment (Legg K., 2012). Especially for small components that require a long life-time, CVD can be a cost-effective alternative to functional chrome plating.

The deposition rate is significantly lower than in the functional chromium trioxide plating process. The deposition rate for functional chrome plating is typically around 60 µm/h versus a maximum of 1.5 µm/h for CVD. Additionally, long times are needed for vacuum generation.

Energy consumption is high due to the vacuum needed. The consumption of electrical energy for the generation of the high-vacuum and plasma is very high compared to the energy consumption of electrodeposition processes like chromium trioxide functional chromium plating.

6.5.4 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 the substances used within this alternative (see Appendix 1.1.5), tungsten, as toxicological worst case, is classified as Flam. Sol. 1, Self-heat. 2, Skin Irrit. 2 and Aquatic Chronic 4. As such, transition from chromium trioxide – which is a non-threshold carcinogen – to thin DLC would constitute a shift to less hazardous substances.

6.5.5 Availability

In general, CVD is a commercially available process. The specific feedback from the consultation showed that at the current R&D stage the technical limitations have not yet been overcome. A minimum of 10 – 15 years is expected to develop a general metallic chrome coating alternative.

6.5.6 Conclusion on suitability and availability for alternative CVD (thin DLC)

Thin DLC coatings are currently not relevant for use as a lifetime running surface coating. Thin CVD processes are technically not feasible and do not represent a suitable alternative to replace functional chrome plating.

CATEGORY 2 ALTERNATIVES

6.6 ALTERNATIVE 6: Thermal spray process - Wire flame spraying

6.6.1 Substance ID and properties

Wire flame spraying is a relatively old process that was developed at the beginning of the 20th century. This technology uses coating material in form of a wire, which is fed continuously into an oxygen-acetylene flame. As a consequence of the heat within the flame (app. 3160 °C), the tip of the wire melts. The melt is removed from the tip of the wire as a droplet by atomising gas. At the same time the melt particles are accelerated to about 200 m/s speed and shot onto the substrate that is to be coated. The particle speed is mainly determined by atomizing gas pressure and speed.

Figure 34 illustrates the scheme of wire flame spraying (left) and the microscopic structure of a wire flame coated substrate (right).

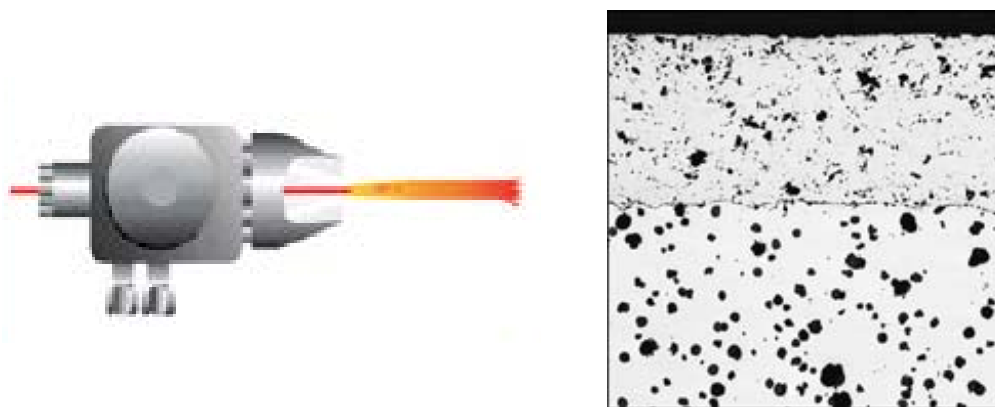


Figure 34: left: Spray gun for wire flame spraying: right: Cross section of wire flame sprayed deposited coating

Source: left: http://pcs.federalmogul.com/ProductLiterature/GOE_PistonRingBrochure_new9853c6bf-e3df-4f05-96df-c5d49c132a3c.pdf, right: Material Specification GOE 200

For the coating of piston rings, molybdenum is used as coating material. Besides molybdenum, acetylene and oxygen are used within the process.

A non-exhaustive overview of general information and the identity of relevant substances used within this alternative and the risk to human health and the environment is provided in Appendix 1.1.6.

6.6.2 Technical Feasibility

Wire flame spraying technology is not used for piston ring coatings in the automotive sector due to serious limitations.

Wear resistance: The general wear resistance of molybdenum coatings by wire flame spraying is too low to for most types of piston rings/engines. Wire flame spraying is usually used for abrasion-resistant coatings, which are not applied for piston rings for automotive applications. Therefore wire flame spraying with molybdenum does not provide the opportunity to replace functional chrome plating technology for piston rings.

Scuff resistance: Due to formation of hard ceramic oxides during spraying and the high melting point wire flame spray coatings with molybdenum show a higher scuff resistance compared to pure chromium coatings.

Hardness: Wire flame spraying with molybdenum leads to coatings that are of inhomogeneous hardness. Those areas with elementary molybdenum provide low hardness whereas the areas covered with the oxide phase provide high hardness. This leads to an average hardness of 480 -1380 HV. Thus the hardness of the wire flame spray coatings with Molybdenum is regarded as not sufficient for most applications focusing on wear resistance.

Corrosion resistance strongly depends on porosity which increases the corrosion exposure area. Porosity of the wire flame spray coatings with molybdenum is not higher than 20 %.

Side face protection: The use of wire flame spray coatings as a side face protection is hardly feasible. The coating would form in a non-uniform way on the side face and the running surface. This would mean that the running surface of every single ring would have to be protected during side face coating in order not to impair the running surface. Because of the roughness of the coated surface, the side faces would have to be extensively machined with a high likelihood of chipping off of the coating.

Assessment overview for Wire Flame sprayed molybdenum coatings				
Wear resistance	Scuff resistance	Hardness	Corrosion resistance	Side face protection

6.6.3 Economic feasibility

Against the background of significant technical failure of wire flame spraying, no quantitative analysis of economic feasibility was conducted.

At the moment equipment for wire flame spraying is only available at one of three plants of F-M. The capacity of the existing site is limited to a small number of rings. In order to be able to replace chromium-based coating technologies large investments are necessary. Besides the expenses for equipment and room for production, also the costs for qualification of personnel need to be taken into account.

6.6.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances (see Appendix 1.1.6) and products reported during the consultation were reviewed for comparison of the hazard profile. Substances used in this process as described above are acetylene, oxygen and molybdenum. Even though molybdenum is “not classified” by a lead dossier of a joint submission for REACH registration, there are other notifications that classify molybdenum as Flam. Sol. 1, Repr.2, Eye Irrit. 2 and STOT RE 1. Therefore molybdenum constitutes the classification worst case. As such, transition from chromium trioxide – which is a non-threshold carcinogen – to one of these substances would constitute a shift to less hazardous substances. The risks of particulate matter and noise need to be considered as well.

6.6.5 Availability

In general, wire flame spraying is a fully developed commercial process. Equipment and material can be obtained commercially from a number of vendors. At Federal-Mogul, this process is industrialized, but used only for niche applications.

6.6.6 Conclusion on suitability and availability for alternative wire flame spraying

Wire flame spraying was assessed with regard to the key parameters, which are to be met in order to replace chromium trioxide derived coatings of piston rings.

Due to low wear resistance, wire flame spray coating is technically feasible for niche applications only.

6.7 ALTERNATIVE 7: Plasma spraying

6.7.1 Substance ID and properties / process description

Plasma spraying is a thermal spray process which uses highly energetic plasma as a heat source. For piston ring applications, coatings with a metal matrix and hard particles are used.

A spray gun for plasma spraying and the cross section of a plasma sprayed coating are shown in **Figure 35**.

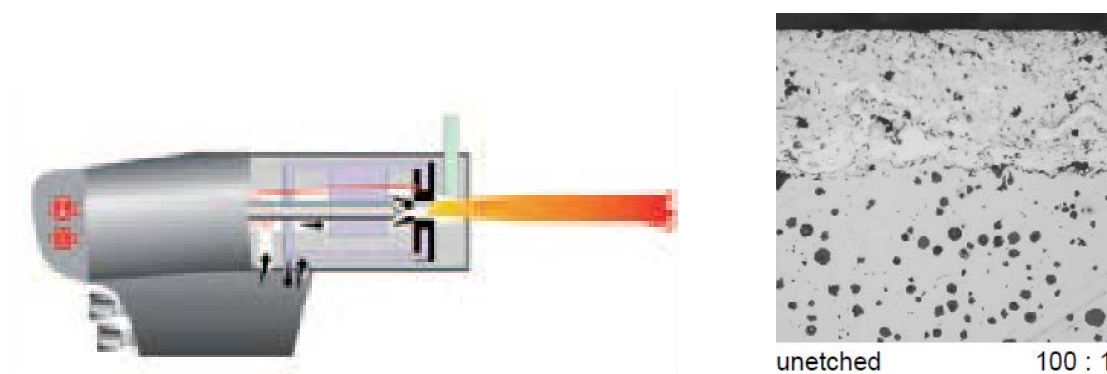


Figure 35 Spray Gun for plasma spraying; right: Cross section of plasma sprayed coating

Source: left: http://pcs.federalmogul.com/productliterature/goe_pistonringbrochure_newa996f640-1e58-4f38-8589-80eff1f9a83f.pdf; right: http://korihandbook.federalmogul.com/en/section_67.htm

The plasma is formed by a high density arc current within the spray gun in the space between cathode and anode that is filled with gases such as hydrogen or argon. The plasma gas is ionised, heated up to 20,000°C and focused as a beam towards the work piece. The coating material in powder form is injected into the plasma beam. The heat of the plasma softens the powder particles, which hit the substrate at high speed and flatten in pancake-shaped “splats”. As they overlay each other, these splats form a continuous coating, merging the boundaries of the individual splats into a coherent coating material. The coatings typically contain pores, oxide inclusions and some unmelted particles.

The microstructural properties of the coating are determined by the coating material and the properties of the plasma stream. The plasma properties depend on nozzle geometry, type of gas and electric arc settings. Typical plasma-sprayed coatings have a high surface roughness after coating, and a rather coarse microstructure with pores, oxide inclusions and un-melted particles. The adhesion is mostly achieved by form fit between coating and base material. In order to improve adhesion, the substrate is normally roughened, for example by sandblasting.

The deposition rate is high, with a powder feed rate of up to 10 kg/h. However, not all of the powder used contributes to forming the coating, as a typically more than half is lost as overspray. Coating thicknesses in the range of several hundred microns can be reached. The surface temperature of the work pieces during deposition reaches between 150 and 400°C.

Thermal spray processes offer a large choice of possible starting powders, gases, types of equipment, coating materials and deposition conditions. The possible powder materials for plasma spraying are similar to HVOF. Plasma-sprayed coatings for piston ring applications are for example the following combinations: molybdenum/chromium carbide, or molybdenum/nickel-chromium/chromium carbide. They all possess a relatively soft matrix with embedded hard particles. The average coating hardness of the different phases together lies within the range of 300 to 600 HV 0.5.

A non-exhaustive overview of general substances information used for plasma sprayed coatings and the risk to human health and the environment caused by these substances, is provided within Appendix 1.1.7

6.7.2 Technical feasibility

Plasma spraying technology is not used for piston ring coatings in the automotive sector due to serious limitations.

Scuff resistance: The scuff resistance for plasma spraying is sufficient.

Liner wear: Plasma coatings usually contain inherent tensile stress caused by melted powder particles. The coatings often have a high amount of ceramics (50 – 70 % by volume carbide). Hard material particles can break out as a consequence of restricted adhesion to the metal matrix which leads to high wear on ring and liner side. Liner wear for plasma sprayed piston rings is too high and thus not a feasible alternative for automotive applications.

Hardness: The average coating hardness of the different phases together lies within the range of 300 to 600 HV 0.5 which is sufficient for automotive applications.

Machinability: Due to the specific process conditions, rings adhere to each other as they usually are clamped on a mandrel to allow a high number of rings to be coated. Therefore, mandrel machining is necessary which is more demanding than post-processing of metallic chrome coatings. The production of high numbers of piston rings is therefore much more elaborate with plasma spraying compared with functional chrome plating.

Adhesion to substrate: The bond between the sprayed coating and the substrate is mostly mechanical whilst metallic chrome coatings adhere to the substrate by attraction forces at an atomic. The adhesive strength to the substrate is potentially lower for the plasma sprayed coating than for the metallic chrome coating which can result in flaking off in the worst case.

Trials with thermal sprayed coatings on cylinder liners consisting of 70% metallic matrix and 30% ceramics for wear protection showed in various engine tests lack of cohesion binding. The Al- and Zr-oxides used as ceramic tribological elements in the tested coatings failed to bind strong enough internally, as well as to the substrate and led to major scuffing events in the engine. Once a peeling off started and the structure is harmed, the hard oxides seem to break off the matrix and cause even further 3-party boundary friction events as they are acting as a “hard grinding element” between the cylinder liner running surface and the ring pack.

Layer thickness: Thermal spray coatings can be readily sprayed up to a layer thickness of 0.5 mm and above and are therefore suitable for coating of piston rings for automotive applications with sufficient coating thicknesses for lifetime running surface coatings.

Corrosion resistance: The porosity of the plasma sprayed coatings is high compared to metallic chrome coatings. In combination with thin layer thickness the susceptibility to corrosion is increased. Susceptibility to corrosion can be increased even with thicker deposits on usually corrosion resistant materials due to porosity.

Geometry of coated parts/Edge Design: The number of designs that can be coated by plasma spraying technology is limited. In general, plasma spraying is a line-of-sight process and parts with complex geometry, for example undercuts, are very difficult to coat, if they can be coated at all.

Coatings of inlaid rings and piston rings with sharp edges can be produced. But the risk of deformation caused by blasting prior to coating and residual stress, which is a consequence of not fully melted powder particles, needs to be taken into account. Blasting before coating is necessary to allow a good adhesion of the material. The production of oil control rings is very complicated.

Side face protection: The use of plasma spray coatings as a side face protection is hardly feasible. The coating would form in a non-uniform way on the side face and the running surface. This would mean that the running surface of every single ring would have to be protected during side face coating in order not to impair the running surface. Because of the roughness of the coated surface, the side faces would have to be extensively machined with a high likelihood of chipping off of the coating.

Assessment overview for Plasma spraying				
Scuff resistance	Liner Wear	Hardness	Wear resistance	Machinability
Adhesion	Layer thickness	Corrosion resistance	Geometry/edge design	Side face protection

6.7.3 Economic feasibility

Against the background of significant technical failure of plasma spraying, no quantitative analysis of economic feasibility was conducted. However, the cost for plasma spraying depends on numerous different factors and these are presented in a qualitative to semi-quantitative way below.

The technology for plasma spraying and functional chrome plating differ fundamentally in the equipment and peripherals. The implementation of plasma spraying requires complex machines and infrastructure equipment. A new coating set-up costs several hundred thousand euros. Another limitation is given by the need of extensive current equipment for self-sustaining the arc current for creating the plasma.

The production costs for plasma spraying are significantly higher due to higher equipment costs increased by set-up costs for each part and the higher costs for post-treatment (grinding and polishing).

6.7.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances (see Appendix 1.1.7) and products reported during the consultation were reviewed for comparison of the hazard profile.

As mentioned above, various different powder materials are used for high velocity processes, for which some substances are confidential business information. As an example, the hazard profile from an often-used coating material is illustrated. Mo-Mo₂C-NiCr is classified as Carc. 2, STOT RE 1, Skin sens.1 in the supplier's safety data sheet.

As such, transition from chromium trioxide – which is a non-threshold carcinogen – would not constitute a shift to significantly less hazardous substances.

6.7.5 Availability

In general, plasma spraying is a fully developed commercial process. Equipment and material can be obtained commercially from a number of vendors. At Federal-Mogul, this process is industrialized and used for specific applications for large bore engines.

6.7.6 Conclusion on suitability and availability for alternative plasma spraying

For the application in piston rings for automotive engines, plasma spraying is not a suitable alternative to functional chrome plating, as it shows clear technical limitations in liner wear and adhesion of the coating to the substrate. Furthermore, in contrast to functional chrome plating, plasma spraying does not allow production of some specific functional design features of piston rings. Therefore plasma spraying is not considered to be an alternative that can replace functional chrome plating of piston rings.

6.8 ALTERNATIVE 8: Trivalent hard chromium deposition

6.8.1 Substance ID and properties / Process description

The trivalent chrome (Cr(III)) plating alternative relates to an electrodeposition process for producing a metallic chrome coating from a trivalent chromium electrolyte. Several trivalent chromium electrolytes for decorative applications are commercially available. The maximum achievable coating thickness from these electrolytes is limited to less than 5 µm. At higher coating thicknesses, the coatings become cracked, porous or badly adherent.

Trivalent chromium electrolytes contain the chromium ions for example as chromium trichloride, chromium sulphate, potassium chromium alum ($\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) or ammonium chromium alum ($\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$). In addition, the electrolytes contain buffer substances like boric acid, citric acid, or aluminium sulphate, and complexing agents, for example ammonium as ammonium chloride, glycine, urea, formic acid or oxalate.

The Cr(III) plating process is based on an electroplating technology like the process with chromium trioxide. However, there are important differences in equipment. Additionally, process control in order to obtain a constant coating quality poses yet unsolved problems.

In contrast to most electroplating processes, the anode and cathode compartments must be separated for the deposition from Cr(III) plating electrolytes to avoid Cr(VI) formation on the anodes. This requires the use of a suitable and robust ion-selective membrane. The presence of Cr(VI) in Cr(III) electrolytes severely deteriorates the deposition.

The use of pulsed current is reported to improve the coating properties, creating the need for special costly rectifiers.

The most important differences in the plating processes come from the chemical properties of Cr(III) itself. The deposition is strongly dependent on the formation of certain complex compounds of Cr(III) which do not only form and decompose as a function of electrolyte composition, temperature and pH value, but in many cases also as a function of electrolyte life time. Therefore, close control and adjustment of the process parameters is indispensable.

One pulse-plating Cr(III) process is reported to have a maximum deposition rate of about 80 µm/h, but only for thin layers (TURI 2012). Current high-performance chromium trioxide functional chrome plating electrolytes can reach a deposition rate of more than 60 µm/h. The temperature of a Cr(III) based electroplating bath is between 20 and 60°C depending on the type of electrolyte. The pH value of the Cr(III) based plating bath is very critical for the coating quality. It changes during the electrodeposition process and has to be kept constant within a small pH range.

Substrates that are reported to have been coated include e.g. iron and its alloys (such as engineering steels, carbon steels, stainless steels, aircraft steels), aluminium and its alloys, copper and its alloys, molybdenum and its alloys and nickel and its alloys. However, coatings deposited from Cr(III)-electrolytes are sometimes seen to show weak adhesion to the substrate, therefore the process seems to be sensitive towards base material pre-treatment.

A non-exhaustive overview of general information of substances used within trivalent chromium plating, as well as the overall risk to human health and the environment is provided in Appendix 1.1.8.

6.8.2 Technical feasibility

General Assessment: An advantage of Cr(III) plating would be that it is closest to a “drop-in” replacement – compared to all other alternatives described in this dossier – for current chromium trioxide process technology as far as process type is concerned. However, due to the need for separated anode and cathode compartments, special rectifiers and the need for online process control, major changes would have to be implemented on existing equipment. As Cr(III) electrolytes contain complexing agents, the waste water treatment would also have to be adapted.

Although the research to generate chromium layers out of Cr(III) compounds in aqueous solutions has been ongoing for more than 40 years, it was only successful in some applications for decorative chrome plating with low coating thicknesses. A Cr(III) plating process as a replacement for technical chromium coatings is not industrially available.

Some results on R&D for Cr(III) metallic chrome coatings with coating thicknesses above 5 µm are available from laboratory-scale research, for example (Bohnet, J., 2009). No results are publicly available on industrial application of Cr(III) based functional chrome plating applications. Large plating technology suppliers are currently investing in research to try to improve the Cr(III) plating process and make it industrially available, but the process is still under research.

Process conditions: Cr(III) baths are much more sensitive to metallic impurities and the acidity of the bath than chromium trioxide baths. Small deviations in these process conditions can strongly influence the deposition success and the layer quality (Legg K., 2003). The process window for Cr(III) plating lies in a very narrow pH range which is difficult to maintain. For chromium trioxide functional chrome plating, pH does not need to be controlled in another way than by keeping the chromium trioxide concentration within the process specification. Consequently, establishing a reliable process for Cr(III) coatings of reproducible quality is challenging and not yet technically feasible.

Wear resistance: Publicly available information from the ECOCHROM project stated that material loss for trivalent plated rapid steel is less than for chromium trioxide plated steel. In a Faville wear test a loss of 72 mg/h was measured for standard chromium trioxide pure chrome coatings compared to about 30 mg/h for Cr(III) (Négré, 2002). The results were measured for a complexed and a reduced Cr(III) solution in laboratory scale. However, there is no wear data for the behaviour of chrome coatings from trivalent electrolytes as piston ring coatings. Therefore it cannot be assumed that they can reach the wear resistance of today’s high-performance chromium coatings or even that of pure chromium coatings from chromium trioxide processes.

Coefficient of friction: There is no data available, but the value is not expected to be better than the coefficient of friction of pure chromium coatings obtained from chromium trioxide electrolytes.

Scuff Resistance: There is no data available, but the value is not expected to be better than the scuff resistance of pure chromium coatings obtained from chromium trioxide electrolytes.

Hardness: A maximally achievable hardness of Cr(III) coatings between 700 and 850 HV is reported (Legg K., 2003), compared to the range for chromium trioxide functional chrome coatings between 900 and 1200 HV.

Machinability: There is no data on the machinability of thick coatings deposited from Cr(III) electrolytes. From the known tendency of such coatings to form macro cracks it can be deduced that machining will be complicated and chipping of the coating is likely.

Adhesion to substrate: Based on the data available, coating adhesion seems to be sensitive to electrolyte and base material. There is no data available on the possibility to plate cast iron, a typical piston ring base material.

Layer thickness: The deposition rate of some electrolytes decreases over longer plating times. The Cr(III) process takes approximately three times longer than the conventional chromium trioxide-based process to achieve the desired thickness (TURI, 2012). A large range for the achievable layer thickness is stated in the literature. (NEWMOA 2003, Legg K., 2003). The maximum literature values of up to 500 µm are not supported by evidence and experimental details. Even if Cr(III) layers up to 500 µm seem to be technically possible at laboratory scale, coating quality decreases with increasing thickness. The required layer thickness cannot be obtained while simultaneously maintaining the layer quality using Cr(III).

Corrosion resistance: Current Cr(III) coatings will not provide corrosion resistance due to their tendency to form macro cracks.

Geometry/Edge Design: There is no piston ring specific data available. Other data (Bohnet, J. 2009) indicates that the current density distribution caused by the part geometry does not only influence coating thickness but also the coating properties and adhesion. Therefore it can be assumed that plating of piston rings will pose problems.

Side Face Plating: There is no data available.

Assessment overview for Plasma spraying						
Process stability	Hardness	Machinability	Adhesion	Layer Thickness	Corrosion resistance	Geometry/ Edge Design

6.8.3 Economic feasibility

As the process of trivalent chromium plating with high coating thicknesses is far from being technically feasible, no quantitative analysis of economic feasibility was conducted.

6.8.4 Reduction of overall risk due to transition to the alternative

As the alternative is not technically feasible, only classification and labelling information of substances reported during the consultation were reviewed for comparison of hazard profile (see Appendix 1.1.8).

Based on the available information on the substances used within this alternative (see Appendix 1.1.8), Cr(III) chloride would be the worst case with a classification as Skin Irrit. 2, Eye Irrit. 2, Acute Tox. In general, the trivalent electroplating processes are less toxic than chromium trioxide plating due to the oxidation state of the chromium. Cr(III) solutions do not pose serious air emission issues, but still pose the problems of disposal of stripping solutions (depending on the type of stripping solution) and exposure of staff to chrome dust during grinding.

In addition, there is a certain risk of Cr(VI) being generated during plating process. This is why appropriate security precaution and process management has to be adopted to prevent the formation of Cr(VI). The bath chemistry typically also comprises a high concentration of boric acid, which is a SVHC substance (toxic for reproduction) included on the candidate list and currently on the 6th recommendation for inclusion in Annex XIV. Therefore, the transition from chromium trioxide to trivalent chromium constitutes a shift to less hazardous substances, but only to a limited extent.

6.8.5 Availability

The electroplating process based on Cr(III) bath chemistry as an alternative for chromium trioxide functional chrome plating is still in the early development stage. Research is ongoing but Cr(III) is neither technically ready nor qualified to replace chromium trioxide functional chrome plating applications. Therefore, it is not commercially available and has not gained market acceptance yet.

To date, there is no solid information on reproducibility and performance in an industrial scale. The extremely narrow process window and new process control of a multitude of parameters are further key challenges. There is no guarantee that this task will be successfully accomplished.

Significant R&D would be needed, which is expected to take another 10 – 12 years to achieve implementation of the alternative if technical performance criteria can be met, which is not the case today.

6.8.6 Conclusion on suitability and availability for alternative trivalent chrome plating

The Cr(III) based electroplating systems do not perform as technically equivalent to chromium trioxide-based products and are therefore not a general alternative at present. The development efforts have shown that the Cr(III) process requires more careful control than the chromium trioxide process due to higher process sensitivity towards the presence of impurities. Today the instable process conditions still lead to unreliable reproducibility and unacceptable microstructure with cracks down to the substrate. This is a major issue that impairs the most important key functionalities concerning the Cr(III) layer properties.

To date there is no proof that Cr(III) performs equally compared to chromium trioxide on the most important key functionalities hardness, wear and corrosion resistance for the applications on piston rings. Thus, further R&D is necessary to ensure process conditions and to meet the requirements of the key functionalities first in laboratory scale and then in functional field tests. Major technology suppliers to the electroplating industry also put forward efforts on researching Cr(III) as functional chrome plating alternative to investigate its eventual maturity; however certainly a further decade is required for R&D.

To date, trivalent chromium plating is not an available and technical feasible alternative to replace chromium trioxide plating.

ASSESSMENT OF ALTERNATIVE PRE-TREATMENTS

6.9 Mineral acids as an alternative pre-treatment

After several alternatives for the main surface treatment have been assessed in the previous chapters, alternatives for pre-treatment using chromium trioxide in the functional chrome plating process are discussed in the following. The purpose of the pre-treatment is the removal of surface residues. As there is no clear demarcation, the term etching is used to cover both etching and pickling as chromium trioxide pre-treatment in the following.

However, the development of a pre-treatment alternative to chromium trioxide depends on the potential alternative for functional chrome plating and is no standalone process. Therefore, no definite alternative can be specified while an alternative for functional chrome plating is being investigated.

6.9.1 Substance ID and properties

Mineral acids are possible alternatives to chromium trioxide in the surface pre-treatment process. A substance that is already in use as a pre-treatment prior to other electroplating processes is sulphuric acid. Other substances like hydrochloric, phosphoric or nitric acid might be alternatives as well.

Mineral acids can be used on their own or in combination with other acids, oxidizing agents, wetting agents or inhibitors.

Nickel strike solutions (usually $\text{NiCl}_2 / \text{HCl}$) can be used as an alternative to reverse etching for many stainless steels, but nickel salts present very strong health and safety issues (CMR classification). They are not discussed here in detail as they are not a preferred alternative.

An overview of general information on substances used within this alternative and the risk to human health and the environment is provided in Appendix 1.2.

6.9.2 Technical feasibility

General Assessment: Pre-treatment is necessary to prepare the surface of the substrates for the subsequent process steps. Adequate preparation of the base metal is a prerequisite: adhesion between the metallic chrome coating and the substrate depends on the force of attraction at an atomic level. The surface of the metal – which is mostly cast iron or hardened high-chromium steel for piston rings – must be absolutely free of contaminants, corrosion and other residuals until the plating process is finished.

Well-controlled etch rate and oxide removal: The current pre-treatment processes for piston rings include a reverse etching process using an aqueous solution of chromium trioxide. It has the advantage that the etch rates can be strictly controlled and over-etching can be avoided, as the chemical etch effect is weak once the current stops. In the etching step, on the one hand, enough material must be removed to create a clean and active surface that guarantees good adhesion. On the other hand, the surface roughness should not be excessively increased, as this would lead to rough coatings. Pre-treatment with chromium trioxide provides surface roughness in the application range as required. Sulphuric acid anodic etching has been used successfully for some applications but excessive chemical attack can be an issue. Mineral acids are typically more aggressive towards metals than chromium trioxide solutions and lead to a higher chemical etch effect at similar concentrations. This effect could be reduced by either making the solution more dilute or by decreasing the process time. However, more dilute solutions are more sensitive towards contaminants and changes in concentration, and shorter process times are more difficult to adhere to, with the risk of over-etching. Both effects decrease process robustness in comparison with reverse etching in chromium trioxide solution.

Suitability for all piston ring materials: For the chromium trioxide pre-treatment processes, suitable etching parameters for all piston ring materials were found by adapting only the electric parameters. The pickling and cleaning steps also work for all piston ring materials. An alternative pre-treatment should also be compatible with all relevant substrates. If alternatives were substrate specific, separate pre-treatment baths with appropriate installation would be required for each material. In order to find a reliable and robust method that works for all materials, substantial research would have to be done.

Sufficient surface activation to ensure coating adhesion: This is the main purpose of the pre-treatment processes. For chromium trioxide-based solution it can be reached in a robust and cost-efficient way. For the development of a surface activation for piston ring materials based on a mineral acid, substantial research would have to be done.

Clamping of parts usable for all process steps: Piston rings are stacked on top of each other and clamped together for running surface plating. They form a cylindrical mandrel that looks like a tube with perforated end covers on both ends. This type of clamping is necessary for both the reverse etching step and the deposition of a uniform coating thickness on the piston ring running surface. It would be quite time-consuming and laborious to open the mandrel between the pre-treatment steps. At the same time, such a mandrel is not easily rinsed, creating a risk of carry-over between baths. Chromium trioxide-based pre-treatment allows the use of the same clamping for all pre-treatment steps without the risk of contamination of the subsequent baths. In the case of a mineral acid based pre-treatment, thorough rinsing would be necessary.

Chemical compatibility: In all current pre-treatment steps, the same substance is used for pre-treatment and main treatment. This is a major advantage for several reasons.

Firstly, no rinsing steps are required. If rinsing between pre-treatment steps was required, significant amounts of water would be needed which need to be adequately treated and discharged. Thus, appropriate water and waste water installations become mandatory. In summary, a diversity of additional equipment need to be implemented which fundamentally changes the existing facility design and require significantly more space.

Secondly, thorough rinsing between etching and plating can impair surface activation due to re-oxidation of the surface. This would lead to a deterioration of coating adhesion to the substrate and thus endanger the purpose of the pre-treatment.

Thirdly, if another substance than chromium trioxide is used in the pre-treatment process, **cross contamination** with the plating bath must be avoided. Minor contaminations with sulphate or chloride are sufficient to make the plating bath content unsuitable for functional chrome plating needs and require to disposal and exchange of the bath content. Cross contamination is especially critical for parts with complex geometry, where residues of the pre-treatment solutions may be trapped. This applies to piston rings clamped up for running surface plating. Therefore, all parts must be thoroughly cleaned in additional working steps. If chromium trioxide is the only substance used for pre-treatment, no such cleaning installations are necessary.

Long-time bath stability/Maintenance: Pre-treatment methods based on mineral acids are common for many electroplating processes of other metals. Therefore no problems concerning bath stability or maintenance are expected.

Analytical methods for process control: Analytical methods for the determination of mineral acids exist and do not normally pose problems. If other substances like wetting agents are included in a pre-treatment bath, methods for determination are often given by the supplier. Therefore, no grave problems are expected.

Conclusions: At the current stage, mineral acid based solutions are technically not feasible as a general alternative to chromium trioxide-based etching for all piston ring materials. Intensive research efforts would be needed to improve their performance.

As the performance of the subsequent functional chrome plating step is strongly linked to the pre-treatment process and to the type and chemical composition of the substrate being processed, the alternative does not currently prepare the surface equivalent to a chromium trioxide-based etching process and does not meet the requirements.

The chemical compatibility between the pre-treatment and the main process is especially important for parts like piston rings clamped up for running surface plating, which are difficult to rinse. The chemistry of a pre-treatment alternative to chromium trioxide depends on the potential alternative for

functional chrome plating and is no standalone process. Therefore, no definite alternative can be specified while an alternative for functional chrome plating is being investigated.

Assessment overview for mineral acids as an alternative pre-treatment					
Well-defined etch rate and oxide removal	Suitability for all piston ring materials	Adhesion to the substrate	Chemical Compatibility	Bath stability/ maintenance/	Analytical process control

6.9.3 Economic feasibility

The economic feasibility of etching with mineral acid on metal substrates was not assessed in detail, as the alternative is not technically feasible.

Switching to a chromium trioxide-free etching alternative would generally necessitate the installation of additional bath equipment for rinsing processes. Changes of the facility design and need for space consuming and expensive additional equipment would be significant.

However, there is no indication that the discussed alternative is not economically feasible.

6.9.4 Reduction of overall risk due to transition to the alternative

As the alternatives are 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 the substances used within this alternative (see Appendix 1.2), nitric acid would be the worst case with a classification as Ox. Liq. 3, Skin Corr. 1A, Met. Corr. 1, Skin Irrit. 2, Eye Dam. 1, STOT SE 3. As such, transition from chromium trioxide – which is a non-threshold carcinogen – to one of these substances would constitute a shift to less hazardous substances.

6.9.5 Availability

To date, the pre-treatment process on ferrous substrates for piston rings is typically conducted with chromium trioxide.

For some applications and substrates, the use of sulphuric acid based solutions is qualified but not as a general replacement for the chromium trioxide pre-treatment. As stated during the consultation, the technical feasibility for etching of metals is not yet equivalent to the current chromium trioxide-based process and further R&D is necessary.

The etching pre-treatment has to be adapted according to the subsequent chromium trioxide-free electroplating alternative, which is also still under R&D. However, etching as a pre-treatment to adequately prepare the surface for the subsequent step is always performed in-line with the functional chrome plating step and it is not a stand-alone process.

As pre-treatment and main treatment using chromium trioxide are closely related, it will take a minimum of 10 – 15 years to develop a general alternative as pre-treatment which meets all requirements - analogous to the time frame expected for functional chrome plating alternatives.

6.9.6 Conclusion on suitability and availability for mineral acids

In summary, the use of chromium trioxide in pre-treatment processes is state of the art for running surface plating of piston rings.

The technical feasibility is not yet equivalent to the current process. Using another substance than chromium trioxide for the pre-treatment process requires significant efforts to clean the parts after the pre-treatment by means of rinsing to avoid cross contamination of the plating bath. Already minor amounts of residues from the treatment solution such as sulphates or chlorides make the bath content unsuitable. If no water supply and water treatment facilities are already in place, this constitutes in combination with required additional bath equipment, a fundamental change of the facility design and demands large additional areas.

The development of a pre-treatment alternative to chromium trioxide depends on the potential alternative for functional chrome plating and is no standalone process. While an alternative for functional chrome plating is investigated, adequate custom-tailored pre-treatments are evaluated in parallel or after the potential alternatives for the main process have been qualified. Therefore, the time needed for R&D and industrial implementation of an alternative are identical for pre-treatment and main treatment, which is a minimum of 10 – 15 years.

7 OVERALL CONCLUSIONS ON SUITABILITY AND AVAILABILITY OF POSSIBLE ALTERNATIVES FOR FUNCTIONAL CHROME PLATING

In this Application for Authorisation, a total of eight different alternatives have been considered for the purpose of Functional Chrome Plating with chromium trioxide for piston rings from automotive application such as in the LVP, LVD, MRD and HD segment. Pre-treatment using chromium trioxide has been assessed separately.

Functional chrome plating involves depositing a layer of metallic chromium on the surface of a metallic component, e.g. ferrous materials ranging from different sorts of low-alloyed cast iron to high-alloyed chromium stainless steels and nitrided base materials. The metallic chrome coating provides the article with high mechanical and wear resistance, good machinability, the possibility to produce various designs and a low coefficient of friction. The process is therefore specified for automotive applications where this combination of performance characteristics is critical. Functional chrome plating using chromium trioxide is therefore used for technical applications or in parts that must perform under demanding environmental conditions that involve high temperatures, repetitive wear and mechanical impact.

Functional chrome plating using chromium trioxide involves immersion of the component in each of a series of treatment baths containing chemical solutions or rinses under specific operating conditions and is normally the final step in the overall surface treatment process. Chromium trioxide is a pre-requisite for the main treatment of functional chrome plating to ensure the highest quality of the product and to meet the requirements of the automotive sector. Chromium trioxide is also used in the pre-treatment process to the substrate. To date, sulphuric acid based solutions are already qualified for some applications and substrates but not as a general replacement for chromium trioxide in the pre-treatment. The time needed for R&D and industrial implementation of an alternative are identical for pre-treatment and main treatment which is a minimum of 10 – 15 years.

Functional chrome plating as it is used by Federal-Mogul does not just comprise pure chrome layers but especially the use of reinforced chrome coatings like CKS and GDC. These coatings are based on the process described before. By embedding aluminium oxide (CKS) or diamond particles (GDC) into the network of cracks, the performance of piston ring coatings with respect to wear, scuff resistance, best performance lifetime expectation and good friction level was significantly increased. CKS and GDC are widely used and represent a benchmark for the introduction of Cr(VI)-free coatings.

Newly developed coatings for piston ring applications such as Thick DLC show promising results when comparing the performance parameters for the coating itself (e.g. wear resistance, coefficient of friction). However, these coatings are clearly no alternative as they cannot be used for special piston ring geometries such as sharp lower running edges, which are often used for oil control rings. **Table 8** provides an overview of the technical deficiencies of all category 1 alternatives. For each alternative, the most important parameters that failed the technical feasibility check are listed.

Table 8: Technical deficiencies of category 1 alternatives.

Alternative		Reasons why alternative will not replace functional chrome plating in all applications
1	Case hardening: nitriding/nitrocarburizing	- Wear resistance insufficient for compression rings for LVD and HD - Scuff resistance insufficient for diesel and high stress petrol engines - Choice of base materials for piston rings severely limited - Sharp lower running edges not feasible due to high tendency of chipping and ring fracture

Alternative		Reasons why alternative will not replace functional chrome plating in all applications
2	High velocity oxygen fuel spraying (HVOF)	- Poor adhesion of the carbides to the substrate → breaks likely to occur - Insufficient tribological behaviour on cast iron cylinders - Very hard carbide coatings on the piston rings generate massive abrasive wear on cylinder liners - Mandrel machining unavoidable - Sharp edges for oil control rings cannot be coated - Side face protection not practicable
3	Physical vapour deposition (PVD) – CrN-based	- High residual and compressive stress can negatively affect/deteriorate the piston ring shape - Sharp lower running edges for oil control rings not feasible - Side face protection not practicable - Size and number of parts that can be coated is physically limited by the need of a vacuum chamber - Experience in some engine projects show limitation of coating strength over lifetime with the result of cylinder scratches and coating damages
4	Hydrogen-free thick diamond-like carbon (DLC) coatings	- Layer thickness limited to 25 µm - Rough surface complicates machining - Sharp lower running edges for oil control rings not feasible - Side face protection not practicable - Size and number of parts that can be coated is physically limited by the need of a vacuum chamber - Immense economic burden for implementation of the process instead of functional chrome plating - Availability of production equipment extremely limited
5	Chemical vapour deposition (CVD) – thin DLC coatings	- Wear resistance inferior to high performance metallic chrome coatings like GDC - Very hard and rough surfaces require extensive post treatment of the coating - Adhesion of the coating to the substrate not as good as for functional chrome plating - Insufficient layer thickness to meet life time requirements - Size and number of parts that can be coated is physically limited by the need of a vacuum chamber - Due to brittleness and tendency to chipping sharp edge design not feasible - Side face protection not practicable

For some applications, technologies like PVD or thick DLC (DuroGlide) as invented by F-M are potential alternatives for the stepwise substitution of functional chrome / CKS / GDC plating. To comply with the requirements of the automotive industry these technologies require further development to be applied for piston rings under the specific engine conditions. Herein, increasing the feasible layer thickness compared to the present state of the art is a central objective for the future development of PVD and DLC technologies. F-M conducts intensive research on these new, alternative coating technologies in order to meet the ring-specific requirements. This is even more important, as the successful implementation of alternative technologies in the automotive industry is to a large extent determined by the technical and/or economical added value an alternative provides to the customer.

Alternatives like PVD and thick DLC are in compliance with the high requirements on functionality, reduction of exhaust emissions and efficiency in consumption (fuel, CO₂) as well as functional chrome plating. Despite this fact, the implementation of these alternative technologies comes along with relevant economic disadvantages like significantly increased product costs. In order to compensate the high product costs, F-M focuses on further research to reduce manufacturing costs

and technical advantages in order to create added value for the customers. In this context, thick DLC is given special attention, as it provides the highest potential regarding a technical added value. The essential prerequisite for an introduction of F-M's thick DLC coating on broad scale is the successful reduction of the manufacturing costs to a reasonable value. To achieve this, innovations are required for the coating process as well as for the technology.

The potential added value that can be achieved for PVD compared with functional chrome plating is rather restricted due to the very good performance of CKS and GDC. Significant improvements in wear resistance of new PVD-coating generations could provide the required added value here. First development results on multi-nano-layer PVD coatings unfortunately did not show promising results concerning performance advantages.

In conclusion, based on experience and with reference to the status of R&D programs, alternatives are not foreseen to be commercially available for key applications and pre-treatment before 12 years after sunset date. This time frame does not take into account the average life cycles of vehicles of about 22 years with at least 10 years of spare part guarantee.

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APPENDIXES

APPENDIX 1 – Information on substances used in alternatives

APPENDIX 1.1 - Electroplating alternatives (main process)

APPENDIX 1.1.1: ALTERNATIVE 1: Case hardening (nitriding/nitrocarburizing)

Table 1: Substance IDs and physicochemical properties.

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Carbon monoxide (mono constituent substance)	Physical state at 20°C and 101.3 kPa	Gaseous (odourless)
EC number	211-128-3	Melting point	-199°C
CAS number	630-08-0	Density	1.18 g/cm ³
IUPAC name	Carbon monoxide	Vapour pressure	20,664,910 hPa (at 25°C)
Molecular formula	CO	Water solubility	21.4 ml/L (at 25°C)
Molecular weight	28.01 g/mol	Flammability	≥ 10.9 % lower flammability limit in air
		Flash Point:	≥ 77.6% upper explosion limit
			-
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Ammonia (mono constituent substance)	Physical state at 20°C and 101.3 kPa	Gaseous (colourless, irritating)
EC number	231-635-3	Melting point	-77.7°C
CAS number	7664-41-7	Density	-
IUPAC name	ammonia	Vapour pressure	8,611 hPa (at 20°C)
Molecular formula	NH ₃	Water solubility	482 g/L (at 25°C)
Molecular weight	17.03 g/mol	Flammability	≥ 16% Lower explosion limit
		Flash Point:	≥ 25% upper explosion limit
			-
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Nitrogen	Physical state at 20°C and 101.3 kPa	Colourless gas
EC number	231-783-9	Melting point	-210.0 °C
CAS number	7727-37-9	Density	1.145 g/L
IUPAC name	nitrogen	Vapour pressure	-
Molecular formula	N ₂	Water solubility	Slightly soluble
Molecular weight	28.013 g/mol	Flammability	Non flammable
		Flash Point:	-

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
Carbon monoxide (CAS 630-08-0) (EC 211-128-3)	Press. Gas Flam. Gas 1 Acute Tox. 3 Repr. 1A STOT RE 1	H220 (extremely flammable gas) H331 (toxic if inhaled) H360D (may damage the unborn child) H372 (causes damage to organs)			Harmonised Classification- Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). Index Number: 006-001-00-2
Ammonia (CAS 7664-41-7) (EC 231-635-3)	Press Gas Flam. Gas 2 Skin Corr. 1B Acute Tox. 3 Aquatic Acute 1	H221 (flammable gas) H314 (causes severe skin burns and eye damage) H331 (toxic if inhaled) H400 (very toxic to aquatic life)			Harmonised Classification- Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). Index Number: 007-001-00-5
Nitrogen (CAS 7727-37-9; EC: 231-783-9)	Press. Gas.	H280	335	Additional notifications are available	Substance is not REACH registered. Not included in the CLP Regulation, Annex VI; Included in C&L inventory
	Ref. Liq. Gas.	H281	182		
	Liq. Gas	H280	41		

APPENDIX 1.1.2: ALTERNATIVE 2: High velocity fuel spraying (HVOF)

Table 1: Substance ID and properties

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	WC/Cr2C3-NiCr	Physical state at 20°C and 101.3 kPa	Solid, metal powder, grey, odourless
EC number	Multiple components	Melting point	Multiple components
CAS number	Multiple components	Density	Multiple components
IUPAC Name	Multiple components	Vapour Pressure	Multiple components
Molecular Formula	WC/Cr2C3-NiCr	Water solubility	Multiple components
Molecular weight	Multiple components	Flammability Flash Point	Multiple components
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Kerosene (petroleum)	Physical state at 20°C and 101.3 kPa	liquid
EC number	232-366-4	Melting point	-49 °C
CAS number	8008-20-6	Density	>= 0.77 <= 0.85 g/cm ³ (15 °C)
IUPAC Name	Kerosene (petroleum)	Vapour Pressure	<1 to 3.7 kPa at 37.8 °C
Molecular Formula	Multiple components	Water solubility	-
Molecular weight	Multiple components	Flammability Flash Point	- 29 - 70°C
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Oxygen	Physical state at 20°C and 101.3 kPa	Gas, colourless/liquid, pale blue
EC number	231-956-9	Melting point	-218.79 °C (-361.82 °F)
CAS number	7782-44-7	Density	1.429 g/L (0°C)
IUPAC Name	molecular oxygen	Vapour Pressure	100k Pa (-183.1 °C)
Molecular Formula	O ₂	Water solubility	7.6 mg·L ⁻¹ (20°)
Molecular weight	31.9988 g/mol	Flammability Flash Point	Non flammable -

Table 2: Hazard classification and labelling overview.

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
WC/Cr2C3-NiCr	Eye Irrit. 2 Skin Sen. 1 Carc. 2 STOT RE 1	H319 H317 H351 H372	-	-	Substance is not REACH registered. Not included in the CLP Regulation, Annex VI; Data from supplier's SDS

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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
Kerosene (petroleum) (CAS: 8008-20-6) (EC: 232-366-4)	Asp. Tox. 1	H304			Harmonised Classification- Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). Index Number: 649-404-00-4
Oxygen (CAS 7782-44-7) (EC 231-956-9)	Press. Gas Ox. Gas 1	H270			Harmonised Classification- Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). Index Number: 008-001-00-8

APPENDIX 1.1.3: ALTERNATIVE 3: Physical vapour deposition (PVD) –CrN-based**Table 1:** Substance ID and physicochemical properties.

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Chromium nitride	Physical state at 20°C and 101.3 kPa	Powder (black)
EC number	246-016-3	Melting point	1,770°C
CAS number	24094-93-7	Density	5.90 g/cm ³
IUPAC name	azanylidynchromium	Vapour pressure	-
Molecular formula	CrN	Water solubility	Insoluble
Molecular weight	66.00 g/mol	Flammability Flash Point:	- -
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Titanium Aluminium Nitride	Physical state at 20°C and 101.3 kPa	Violet/black coloured coating about 0.0001 thick, odourless
EC number	-	Melting point	-
CAS number	Not available for Titanium Aluminium Nitride (TiAlN) 25583-20-4 (Titanium Nitride; TiN)	Specific gravity (60 °F)	approximately 5.0-6.0
IUPAC name	-	Vapour pressure	-
Molecular formula	AlTiN	Water solubility	insoluble
Molecular weight	-	Flammability Flash Point	Non flammable -
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Nitrogen	Physical state at 20°C and 101.3 kPa	Colourless gas
EC number	231-783-9	Melting point	-210.0 °C
CAS number	7727-37-9	Density	1.145 g/L
IUPAC name	nitrogen	Vapour pressure	-
Molecular formula	N ₂	Water solubility	Slightly soluble
Molecular weight	28.013 g/mol	Flammability Flash Point:	Non flammable -

Table 2: Hazard classification and labelling overview.

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
Chromium nitride (CAS 24094-93-7)	Not classified		3		Pre registered substance;

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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
(EC 246-016-3)					Notified Classification and labelling according to CLP criteria.
Aluminium titanium nitride (CAS 148793-50-4)	According to suppliers' SDS, the following hazard statements are given Short term exposure: Metallic taste; nausea; tightness of chest, fever; irritation of eyes, nose, throat and skin; loss of consciousness/death due to welding gases or lack of oxygen				Substance is not REACH registered. Not included in the CLP Regulation, Annex VI; Data from supplier's SDS
Nitrogen (CAS 7727-37-9; EC: 231-783-9)	Press. Gas.	H280	335	Additional notifications are available	Substance is not REACH registered. Not included in the CLP Regulation, Annex VI; Included in C&L inventory
	Ref. Liq. Gas.	H281	182		
	Liq. Gas	H280	41		

APPENDIX 1.1.4: ALTERNATIVE 4: Hydrogen-free DLC coatings (thick DLC)**Table 1:** Substance ID and physicochemical properties.

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Chromium	Physical state at 20 °C and 101.3 kPa	Solid brittle, hard, metallic
EC number	231-157-5	Melting point	1863 °C
CAS number	7440-47-3	Density	7.2 g/m ³
IUPAC name	Chromium	Vapour pressure	-
Molecular formula	Cr	Water solubility	-
Molecular weight	51.9961 g/mol	Flammability Flash Point:	Non flammable
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Carbon	Physical state at 20°C and 101.3 kPa	Solid, fibre, odourless, organic
EC number	231-153-3	Melting point	>3500°C
CAS number	7440-44-0	Density	1.78 g/cm ³
IUPAC name	methane	Vapour pressure	-
Molecular formula	C	Water solubility	-
Molecular weight	12.0107 g/mol	Flammability Flash Point	Highly flammable if powdered

Table 2: Hazard classification and labelling overview.

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
Chromium (EC: 231-157-5; CAS: 7440-47-3)	Not classified		644	Additional notifications are available	REACH registered; Not included in the CLP Regulation Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation).
	Skin Sens.1 Resp. Sens. 1	H317 H334	362		
	Eye Irrit.2	H319	355		
	Aquatic Acute 1 Aquatic Chronic 4	H410 H410	92		
	Skin Irrit. 2 Eye Irrit. 2 Muta. 2 Carc. 2 STOT SE 2 STOT RE 2	H315 H319 H341 H351 H371 H373	2		
	Not classified		751		REACH registered;

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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
Carbon (EC: 231-153-3; CAS: 7440-44-0)	Eye Irrit. 2 STOT SE 3	H319 H355	748	Additional notifications are available	Not included in the CLP Regulation Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation).
	Self-heat. 2	H252	60		
	Skin Irrit. 2 Eye irrit. 2	H315 H319	4		
	Self-heat. 2 STOT RE 2	H252 H373 (cardiovascular)	4		
	Acute Tox 2	H300	3		

APPENDIX 1.1.5: ALTERNATIVE 5: Chemical vapour deposition (CVD) – thin DLC**Table 1:** Substance IDs and physicochemical properties.

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Acetylene	Physical state at 20°C and 101.3 kPa	Gaseous, organic, colourless
EC number	200-816-9	Melting point	-80.7 °C
CAS number	74-86-2	Density	0.73 g/cm ³ (-84 °C)
IUPAC name	acetylene	Vapour pressure	4535 kPa (22 °C)
Molecular formula	C ₂ H ₂	Water solubility	1200 mg/L (20 °C)
Molecular weight	26.03728 g/mol	Flammability Flash Point	Flammable -18.15 °C
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Tungsten	Physical state at 20°C and 101.3 kPa	Solid, grey white, metal
EC number	231-143-9	Melting point	3422 °C (1013 hPa)
CAS number	7440-33-7	Density	19.26 g/cm ³ (20 °C)
IUPAC name	tungsten	Vapour pressure	0.1 Pa (3000 °C)
Molecular formula	W	Water solubility	-
Molecular weight	183.84 g/mol	Flammability Flash Point	Highly flammable when finely divided

Table 2: Classification and labelling of relevant substances.

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
Acetylene (EC: 200-816-9; CAS: 74-86-2)	Press. Gas Flam. Gas 1	H220			Harmonised Classification- Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). Index Number: 601-015-00-0
Tungsten (EC: 231-143-9; CAS: 7440-33-7)	Flam. Sol. 1 Self-heat. 2	H228 H252	246		REACH registered; Not included in the CLP Regulation Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation).
	Flam. Sol. 1 Skin Irrit. 2 Eye Irrit. 2	H228 H315 H319	24	Additional notifications are available	
	Aquatic Chronic 4	H413	15		

APPENDIX 1.1.6: ALTERNATIVE 6: Thermal spray process- Wire flame spraying**Table 1:** Substance ID and properties for an exemplary molybdenum coating

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Molybdenum	Physical state at 20°C and 101.3 kPa	Solid, powder, metallic, black to silvery, odourless
EC number	231-107-2	Melting point	2617 °C
CAS number	7439-98-7	Density	10.18 g/cm ³ (20°C)
IUPAC Name	Molybdenum	Vapour Pressure	1 Pa at 2469 °C (solid)
Molecular Formula	Mo	Water solubility	> 6 < 12 mg/L (20 °C)
Molecular weight	95.96 g/mol	Flammability Flash Point	Non flammable -
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Acetylene	Physical state at 20°C and 101.3 kPa	Gaseous, organic, colourless
EC number	200-816-9	Melting point	-80.7 °C
CAS number	74-86-2	Density	0.73 g/cm ³ (-84 °C)
IUPAC Name	acetylene	Vapour pressure	4535 kPa (22 °C)
Molecular Formula	C ₂ H ₂	Water solubility	1200 mg/L (20 °C)
Molecular weight	26.03728 g/mol	Flammability Flash Point	Flammable -18.15 °C
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Oxygen	Physical state at 20°C and 101.3 kPa	Gas, colourless/liquid, pale blue
EC number	231-956-9	Melting point	-218.79 °C (-361.82 °F)
CAS number	7782-44-7	Density	1.429 g/L (0°C)
IUPAC Name	molecular oxygen	Vapour Pressure	100k Pa (-183.1 °C)
Molecular Formula	O ₂	Water solubility	7.6 mg·L ⁻¹ (20°)
Molecular weight	31.9988 g/mol	Flammability Flash Point	Non flammable -

Table 2: Hazard classification and labelling overview.

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
Molybdenum (CAS 7439-98-7) (EC 231-107-2)	Not Classified		413		Classification comes from a lead dossier of a REACH registration joint submission
	Flam. Sol.1	H228	302	Additional notifications are available	
	Repr. 2	H361	299		
	Flam. Liq. 2	H225	91		
	Flam. Sol. 2	H228	8		
	Eye Irrit. 2	H319	5		
	STOT RE 1	H372	1		
Acetylene (EC: 200-816-9; CAS: 74-86-2)	Press. Gas Flam. Gas 1	H220			Harmonised Classification- Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). Index Number: 601-015-00-0
Oxygen (CAS 7782-44-7) (EC 231-956-9)	Press. Gas Ox. Gas 1	H270			Harmonised Classification- Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). Index Number: 008-001-00-8

APPENDIX 1.1.7: ALTERNATIVE 7: Plasma spraying**Table 1:** Substance ID and properties

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Cr3C2/Mo/NiCr	Physical state at 20°C and 101.3 kPa	Gray powder, solid
EC number	Multiple components	Melting point	Multiple components
CAS number	Multiple components	Density /Specific gravity	9.3
IUPAC Name	Multiple components	Vapour Pressure	Multiple components
Molecular Formula	Cr3C2/Mo/NiCr	Water solubility	insoluble
Molecular weight	Multiple components	Flammability Flash Point	Multiple components
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Mo/Mo2C/NiCr	Physical state at 20°C and 101.3 kPa	Multiple components
EC number	Multiple components	Melting point	Multiple components
CAS number	Multiple components	Density	Multiple components
IUPAC Name	Multiple components	Vapour Pressure	Multiple components
Molecular Formula	Mo/Mo2C/NiCr	Water solubility	Multiple components
Molecular weight	Multiple components	Flammability Flash Point	Multiple components

Table 2: Hazard classification and labelling overview.

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
Cr3C2/Mo/NiCr	Dust and fumes can cause irritation of the eyes, nose, throat, and respiratory tract. Inhalation of nickel is suspected of causing nasal and/or lung cancer. Skin contact cause irritation or allergic skin rash due to nickel and/or chromium sensitization. Aside from isolated reports in the Russian Literature suggesting an association between molybdenum exposure and pulmonary and joint disorders (Gout-like condition), there are no recognized long term effects attributed to industrial exposure to molybdenum. Carcinogenic Assessment (NTP Annual Report, IARC Monographs, Others): The National Toxicology Program (NTP) found there was sufficient evidence of carcinogenicity of nickel in experimental animals and limited evidence for carcinogenicity of nickel in humans. The International Agency for Research on Cancer (IARC) found there was inadequate evidence that metallic nickel is carcinogenic to humans but sufficient evidence that it is carcinogenic to experimental animals. IARC concluded that metallic nickel is possibly carcinogenic to humans (Group 2B). The NTP and IARC found there was inadequate data for the carcinogenicity of metallic chromium and trivalent chromium compounds (Group 3). Hexavalent chromium compounds, which may be formed during thermal spray operations, are classified as carcinogenic to				Substance is not REACH registered. Not included in the CLP Regulation, Annex VI; Data from supplier's SDS

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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
	humans (Group 1). Nickel and chromium have not been classified as a known or suspected carcinogen by OSHA.				
Mo/Mo2C/NiCr	Carc. 2 STOT RE1 Skin sens. 1	H351 H372 H317	-	-	Data from supplier's SDS

APPENDIX 1.1.8: ALTERNATIVE 8: Trivalent hard chromium**Table 1:** Substance ID and physicochemical properties

Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Chromium trichloride hexahydrate	Physical state at 20°C and 101.3 kPa	Solid (green)
EC number	-	Melting point	80-83°C
CAS number	10060-12-5	Density	-
IUPAC name	Chromium(III) chloride hexahydrate	Vapour pressure	-
Molecular formula	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	Water solubility	590 g/L (at 20°C)
Molecular weight	266.45 g/mol	Flammability Flash point	Non flammable -
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Boric acid (mono constituent substance)	Physical state at 20°C and 101.3 kPa	Solid (crystalline, odourless)
EC number	233-139-2	Melting point	No melting point detected below 1,000°C
CAS number	10043-35-3	Density	1.49 g/cm ³
IUPAC name	Boric acid	Vapour pressure	$9.90 \cdot 10^{-8}$ kPa (25 °C)
Molecular formula	$\text{B}(\text{OH})_3$	Water solubility	48.40 g/L (20°C, pH = 3.6)
Molecular weight	61.83 g/mol	Flammability Flash point	Non flammable -
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Chromium potassium bi(sulphate)	Physical state at 20°C and 101.3 kPa	Solid (purple red)
EC number	-	Melting point	89.0°C
CAS number	7788-99-0	Density	1.83 g/cm ³
IUPAC name	Chromium(3+) potassium sulfate hydrate (1:1:2:12)	Vapour pressure	-
Molecular formula	$\text{CrKS}_2\text{O}_8 \cdot 12 \text{H}_2\text{O}$	Water solubility	250 g/L
Molecular weight	499.4 g/mol	Flammability Flash Point	Non flammable -
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Formic acid (mono constituent substance)	Physical state at 20°C and 101.3 kPa	Liquid
EC number	200-579-1	Melting point	4.0°C
CAS number	64-18-6	Density	1.22 g/cm ³ (at 20°C)
IUPAC name	Formic acid	Vapour pressure	42.71 hPa (20°C)
Molecular formula	CH_2O_2	Water solubility	Miscible in any ratio

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Parameter	Value	Physicochemical properties	Value
Molecular weight	46.0 g/mol	Flammability Flash Point	Flammable 49.5°C (at 1,013 hPa)
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Ammonium sulfamidate	Physical state at 20°C and 101.3 kPa	Solid (colourless)
EC number	231-871-7	Melting point	131-135°C
CAS number	7773-06-0	Density	1.00 g/cm ³
IUPAC name	Ammonium sulphamate	Vapour pressure	-
Molecular formula	H ₆ N ₂ O ₃ S	Water solubility	1,666 g/L
Molecular weight	114.12 g/mol	Flammability Flash Point	Non flammable -
Parameter	Value	Physicochemical properties	Value
Chemical name and composition	Ammonium chloride	Physical state at 20°C and 101.3 kPa	Solid (crystalline)
EC number	235-186-4	Melting point	340°C (sublimation)
CAS number	12125-02-9	Density	1.53 g/cm ³ (at 20°C)
IUPAC name	Ammonium chloride	Vapour pressure	-
Molecular formula	NH ₄ Cl	Water solubility	283 g/L (25°C)
Molecular weight	53.5 g/mol	Flammability Flash Point	Non flammable -

Table 2: Classification and labelling of relevant substances.

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
Chromium trichloride hexahydrate (CAS 10060-12-5)	Skin Irrit. 2 Eye Irrit. 2 STOT SE 3	H 315 (causes skin irritation) H 319 (causes serious eye irritation) H 335 (may cause respiratory irritation)	30		Substance is not REACH registered. Not included in the CLP Regulation, Annex VI; Included in C&L inventory
	Acute Tox. TOX 4	H 302 (harmful if swallowed)	24		
Boric acid (CAS 10043-35-3; EC 233-139-2)	Repr. 1B	H360FD			Harmonised classification- Annex VI of Regulation (EC) No 1272/2008 Included in CLP Regulation, Annex VI (index number 005-007-00-2)
Chromium potassium	Skin Irrit. 2 Eye Irrit. 2	H 315 (causes skin irritation)	5		Pre-registered substance

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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
bi(sulphate) dodecahydrate (CAS 7788-99-0)		H 319 (causes serious eye irritation)			Not included in the CLP Regulation, Annex VI; Included in C&L inventory
Formic acid (CAS 64-18-6 (EC 200-579-1)	Skin Corr 1A	H 314 (causes severe skin burns and eye damage)		Skin Corr. 1A; H314: $C \geq 90\%$ Skin Corr. 1B; H314: $10\% \leq C < 90\%$ Skin Irrit. 2; H315: $2\% \leq C < 10\%$ Eye Irrit. 2; H319: $2\% \leq C < 10\%$	Harmonised classification- Annex VI of Regulation (EC) No 1272/2008 Included in CLP Regulation, Annex VI (index number 607-001-00-0);
Ammonium sulphamidate (CAS 7773-06-0) (EC 231-871-7)	Acute Tox. 4	H302 (harmful if swallowed)	49		Pre-registered Substance Not included in the CLP Regulation, Annex VI; Included in C&L inventory
	Not classified	-	46		
	Acute Tox. 4 Aquatic Acute 1	H 302 (harmful if swallowed) H 400 (very toxic to aquatic life)	23		
Ammonium chloride (CAS 12125-02-9) (EC 235-186-4)	Acute Tox 4 Eye Irrit. 2	H 302 (harmful if swallowed) H 319 (causes serious eye irritation)			Harmonised classification- Annex VI of Regulation (EC) No 1272/2008 Included in CLP Regulation, Annex VI (index number 017-014-00-8);

APPENDIX 1.2 - Pre-treatments: mineral acids

Table 1: Substance IDs and physicochemical properties are presented (not exhaustive):

Parameter	Value	Physico-chemical properties	Value
Chemical name and composition	Sulphuric acid (mono constituent substance)	Physical state at 20°C and 101.3 kPa	Liquid (odourless)
EC number	231-639-5	Melting point	10.4-10.5°C (pure sulphuric acid)
CAS number	7664-93-9	Density	1.83 g/cm ³ (20°C, pure sulphuric acid)
IUPAC name	Sulphuric acid	Vapour pressure	0.49 hPa (20°C)
Molecular formula	H ₂ SO ₄	Water solubility	Miscible with water
Molecular weight	98.08 g/mol	Flammability Flash point	Non flammable -
Parameter	Value	Physico-chemical properties	Value
Chemical name and composition	Orthophosphoric acid (mono constituent substance)	Physical state at 20°C and 101.3 kPa	Solid (crystalline, if no water attached)
EC number	231-633-2	Melting/freezing point	41.1 °C (101 kPa)
CAS number	7664-38-2	Density	1.84 g/cm ³ (38°C)
IUPAC name	Phosphoric acid	Vapour pressure	80 Pa (25°C, extrapolated)
Molecular formula	H ₃ PO ₄	Water solubility	5,480g/ L (cold water, pH= 0.5)
Molecular weight	98.00 g/mol	Flammability Flash point	Non flammable -
Parameter	Value	Physico-chemical properties	Value
Chemical name and composition	Nitric acid (mono constituent substance)	Physical state at 20°C and 101.3 kPa	Liquid (fumes in moist air)
EC number	231-714-2	Melting/freezing point	- 41.60 °C
CAS number	7697-37-2	Density	1.51 g/cm ³ (20°C)
IUPAC name	Nitric acid	Vapor pressure	9.00 kPa (25°C)
Molecular formula	HNO ₃	Water solubility	> 1,000g /L (20°C, pH= -1)
Molecular weight	63.01 g/mol	Flammability Flash point	Non flammable -
Parameter	Value	Physico-chemical properties	Value
Chemical name and composition	Chromium(III) sulphate	Physical state at 20°C and 101.3 kPa	Solid
EC number	233-253-2	Melting point	90 °C
CAS number	10101-53-8	Density	3.10 g/cm ³ (anhydrous)
IUPAC name	Chromium(III) sulphate	Vapour pressure	-

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Parameter	Value	Physico-chemical properties	Value
Molecular formula	Cr ₂ (SO ₄) ₃	Water solubility	Insoluble (anhydrous). Soluble as hydrate.
Molecular weight	392.18 g/mol	Flammability Flash point	Non-flammable -
Parameter	Value	Physico-chemical properties	Value
Chemical name and composition	Iron(II)-sulphate	Physical state at 20°C and 101.3 kPa	Solid
EC number	231-753-5	Melting point	> 300°C (decomposes)
CAS number	7720-78-7	Density	3.65 g/cm ³
IUPAC name	Iron(2+) sulphate	Vapour pressure	-
Molecular formula	FeSO ₄	Water solubility	Very soluble (>10,000 mg/L)
Molecular weight	151.9 g/mol	Flammability Flash point	Non flammable -

Table 2: Hazard classification and labelling overview

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	
Sulphuric acid (CAS 7664-93-9) (EC 231-639-5)	Skin Corr. 1A Met. Corr. 1	H314 (Causes severe skin burns and eye damage) H290 (may be corrosive to metals)	n/a	Specific Concentration limits: Skin Corr. 1A: $C \geq 15\%$, H314 Skin Irrit. 2: $5\% \leq C < 15\%$, H315 Eye Irrit. 2: $5\% \leq C < 15\%$; H319	REACH registered; Included in CLP Regulation, Annex VI (index number 016-020-00-8);	
Phosphoric acid (CAS 7664-38-2) (EC 231-633-2)	Skin Corr. 1B	H314 (Causes severe skin burns and eye damage)	n/a	Legal classification.	REACH registered; Included in CLP Regulation, Annex VI (index number 015-011-00-6);	
	Met. Corr. 1	H290 (May be corrosive to metals)	n/a	Additional self-classification according to REACH registration;		
Nitric acid (CAS 7697-37-2) (EC 231-714-2)	Ox. Liq. 3	H272 (May intensify fire; oxidizer)	n/a		REACH registered; Included in CLP Regulation, Annex VI (index number 007-004-00-1)	
	Skin Corr. 1A	H314 (Causes severe skin burns and eye damage)				
	Met. Corr. 1	H290 (May be corrosive to metals)		Additional classification according to REACH registration.		
	Not classified	-	257	Classification notified to the C&L inventory.		
	Skin Irrit. 2	H315 (Causes skin irritation)	271	Classification notified to the C&L inventory.		
	Eye Dam. 1	H318 (Causes serious eye damage)				

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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
	STOT SE 3	H335 (May cause respiratory irritation)		Further 163 notifiers classified the substance as Eye Dam. 1 only.	
Chromium sulphate (CAS 10101-53-8) (EC 233-253-2)	Not classified	-	1103	1103 notifiers did not classify the substance.	Currently not REACH registered; Not included in the CLP Regulation, Annex VI; Included in C&L inventory
Iron(II) sulphate (CAS 7720-78-7) (EC 231-753-5)	Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2	H302 (harmful if swallowed) H315 (causes skin irritation) H319 (causes serious eye irritation)	-		Reach registered substance; Harmonised classification- Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). (Index number: 026-003-00-7)

APPENDIX 2– 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: <http://echa.europa.eu/de/>
2. ChemSpider internet site: <http://www.chemspider.com>
3. Merck SDS: www.merckgroup.com
4. Sigma Aldrich SDS: <http://www.sigmaaldrich.com>
5. READE internet site: <http://www.reade.com>
6. Chemie.de internet site: <http://www.chemie.de>
7. Alfa Aesar SDS: <http://www.alfa.com/content/msds/German/14510.pdf>
8. Carl Roth SDS: <http://www.carlroth.com>
9. MAK Collection for Occupational Health and Safety: <http://onlinelibrary.wiley.com>
10. Chemical Book internet site: <http://www.chemicalbook.com>
11. Merck SDS: <http://www.merck-performance-materials.com>
12. Analytyka SDS: <http://www.analytyka.com>
13. Airgas.com internet site: <http://www.airgas.com/msds/001069.pdf>
14. Air Liquide internet site: <http://encyclopedia.airliquide.com>
15. Air Liquide SDS: <http://www.airliquide.de>
16. Praxair Surface Technology internet site: www.praxairsurfacetechologies.com
17. Sciencelab internet site: www.sciencelab.com
18. National Center for Biotechnology Information: <https://www.ncbi.nlm.nih.gov/pccompound>