TripleHard® by Savroc

High performance trivalent chromium coating – an alternative for Chromium Trioxide

Introduction

TripleHard® is based on an innovation discovered in Kuopio, Finland, back in 2012. The discovery of the technology was inspired by a vision of a better and less harmful chrome plating method free of Chromium Trioxide (CrVI). After several years of research and development, the technology is on the verge of a breakthrough. Commercialization and industrialization is in progress, and various laboratory and field tests have been successfully concluded by our customers. TripleHard® has outperformed CrVI based solutions both in terms of technical performance and overall costs. The current TripleHard process is also now free of boric acid.

Currently, industrial chrome plating companies and end users are searching for alternatives to CrVI. Trivalent chromium has shown most potential in replacing CrVI and is an increasingly used method in decorative chrome plating. The trivalent chromium process is well-known and has been investigated for many years, but until recently, the properties of trivalent chromium have not been able to reach levels required in functional applications. Other methods, such as PVD or thermal spraying methods, require large expensive investments in facilities and possibly a complete redesign of the product and manufacturing method. Trivalent chrome plating is the best and most reasonable alternative to hexavalent hard chrome plating as it as it is very similar and does not require large changes – it is a drop-in solution.

However, the properties, such as hardness, wear resistance and corrosion resistance of trivalent chromium can be enhanced significantly with rather simple changes in the plating process through our TripleHard® approach by changing the chemical composition. This method called TripleHard®, which is patented worldwide (18 patents in December 2020 and now exists in three different versions, enables the use of trivalent chromium in functional or even decorative applications. Without the TripleHard® process trivalent chromium has not been able to pass highly demanding wear tests. After the process, the properties are superior to CrVI based processes, and most importantly, the plating process is much safer for the workers and for the environment. The new technology enables a safe environment wherever the business and production itself is located. All industries must be responsible of keeping their whole production line, from beginning to final product, safe for both people and the environment. The answer is not to transfer manufacturing outside the EU towards less strict health and environment regulations.

Process and infrastructure

The trivalent electrolytic process can exploit a similar infrastructure as CrVI. The basic concept is more or less the same; degreasing, activation, optional nickel-plating and chromium plating. Between each step follows a rinsing step with deionized water to prevent contamination. The plating tank can be made of e.g. titanium, titanium with HDPE lining or HDPE. The usage of steel should be minimized, as it corrodes and contaminates the chromium bath. Also traces zinc and copper are harmful for trivalent chromium process and the usage of them should be avoided near the bath. Anodes can be made from either graphite or Ti-MMO (Titanium-mixed metal oxide). Standard rectifiers and such can be used. The conversion of CrVI plating line to trivalent line is rather simple and does not require a complete makeover. In fact, as hexavalent process fumes and ventilation air needs to be filtered and purified, in trivalent process this is not necessary as the fumes are not as harmful and standard air ventilation is sufficient.

Electroplating process

The working temperature of the bath is currently 30-50°C. The efficiency of trivalent process is better than in hexavalent chroming, because of less complex reduction process of trivalent chromium. More energy is needed for CrVI to become reduced and to form a chrome plating compared to trivalent process. Traditionally, the growth rate has been lower than with CrVI, but new sulfamate-based trivalent chromium baths have exceeded the rates of CrVI. Another advantage of the new sulfamate-based chemistry is that they contain no boric acid. These new types of bath are being investigated thoroughly by chemical companies and research institutes.

TripleHard® can be applied directly on many materials without a nickel underlayer. If corrosion resistance is a primary requirement, a nickel-strike or electroless nickel can be applied before TripleHard® layer, although corrosion resistance is good even without a nickel underlayer. Nickel-underlayer also expands the range of materials that TripleHard® can be plated onto. Usually, a TripleHard® layer between 5-100 µm is suitable for majority of applications. The most typical layer thickness is from 5 to 30 µm, as it provides the mechanical properties required and the process is stable. It's essential to note that a nickel layer is also used with CrVI when a superior corrosion resistance is required, however in comparison the TripleHard® method requires less use of nickel.

Mechanical properties

Mechanical properties such as hardness, friction, wear and corrosion resistance and adhesion of the coating are crucial for functional chromium plating. In this chapter the properties of TripleHard®

chromium coating are investigated and compared to hard chromium and other alternative coating methods. These results are confirmed by multiple customers and research institutes in addition to Savroc's own tests.

Hardness

Hardness is defined as the materials ability to resist plastic deformation, such as indentation, scratching, abrasion or such. It is a vital property in many industrial applications, such as cylinder rods, shock absorbers, ball valves, etc. It can be stated that hardness increases materials resistance to either friction or erosion, and therefore it is an important factor when selecting a surface treatment or coating [6]. The hardness of TripleHard® coating is based on the structure, compounds and phases in the chromium layer. The TripleHard® meets the hardness achieved typically with Chromium Trioxide.
TripleHard® can also withstand heat and thermal shocks well.

Wear resistance

Excellent wear resistance is partly due to the high hardness of TripleHard®, but other factors affect it too. A smooth surface provides also a low friction. Pin-on-rod tests are often used in internal testing to investigate the wear resistance of coating. In this test a hard metal ball is being pressed by load on a rotating rod. Similar but harsher test, block-on-ring (BOR), is used to determine the wear resistance of coatings, especially in linkage pins [8]. BOR-test is a commonly used method in the industry to investigate wear resistance of materials and coatings. In this test, TripleHard® was compared to use of CrVI. The part treated with a CrVI method did not last until the end of the test, which is indicated by the spike in friction graph. TripleHard® however lasted until the end of test.

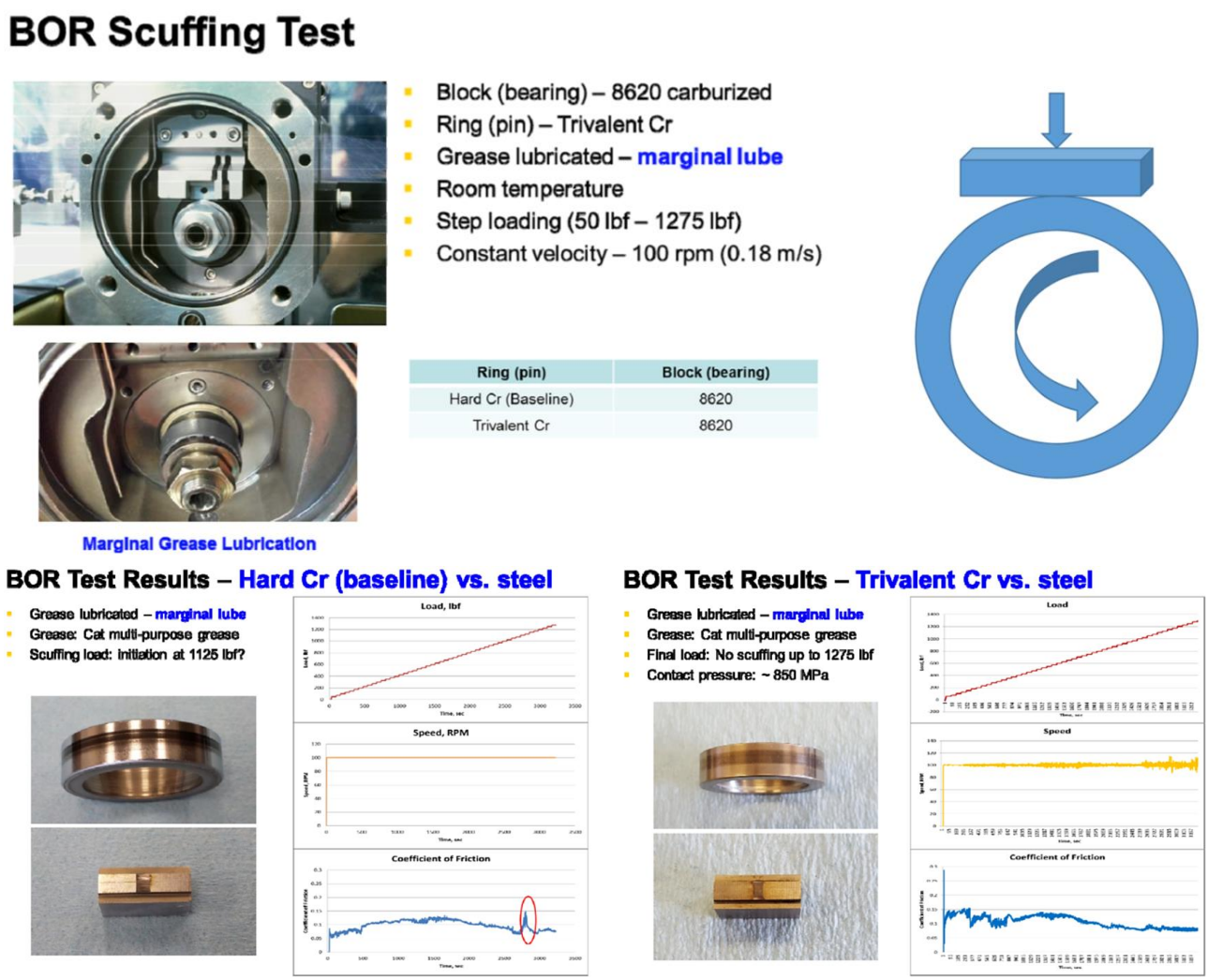

Figure 1. *Block-on-ring test and results. TripleHard coating lasted until the end of the test while CrVI failed before the end..*

Taber-test is a standardized test to investigate wear and abrasion resistance of materials [9]. This test was performed by an external research institute, and TripleHard® displayed excellent results. Wear index of TripleHard® coating after 10000 cycles with 1 kg load with CS-10 wheel was 1.03, significantly lower compared to hard chromium (2.0). In the test average Taber wear index for TripleHard® was 1.0 mg loss per 1000 cycles.

Table 1*. Taber wear test results of different coatings (a smaller number is a better value).*

Test	TripleHard	CrVI	Electroless nickel	Electroless nickel + thermal treatment 400C
Taber wear index ***CS10, 1 kg, 10000 cycles***	1	2	16	9

Corrosion and acid resistance

TripleHard® coating withstands corrosion well. In terms of corrosion resistance it is at least as good a CrVI beased hard chrome.

Proof of technology

TripleHard® has already been industrially approved in many applications and has been taken into use in replacing hard chromium, for example in ball valves, hydraulic rods, and wear parts. The process itself has been working in an industrial scale for more than 5 years at Tecnocrom Industrial S.A. in Barcelona, Spain. The TripleHard® plating process has also been tested in a continuous horizontal plating line and the preliminary results have shown that there are no obstructions for the process to work similarly as CrVI plating. Table 2 below represents the proof of technology and current situation in different applications.

Table 2. *Proof of technology and current situation of TripleHard*

Application	Tests	Status
Hydraulic cylinders	Corrosion, wear, sealing, bending, variety of testing	Lifetime tests passed Industrial production
Valve components (ball, seal rings, cylinder rods and tubes)	Wear, Sealing properties, corrosion	Field operational tests passed Industrial production
Gun barrels	Shooting tests, Corrosion, wear, thermal shocks	Shooting tests passed
Linkage pins	Galling resistance	Lab tests passed, field test running
Automotive brake parts	Wear, Corrosion	Lab tests passed
Shock absorbers	Corrosion, wear, bending, cracking	Lab tests passed
Wear parts	Wear resistance	Industrial production
Undercarriage components	Galling resistance	Lab tests passed

Availability and viability for Husqvarna

Savroc has patented TripleHard® technology. The technology and chemicals are available through licensing agreements. A conversion of an existing electroplating facility to use TripleHard® will typically take less than a week. In its AoA Husqvarna argues that: *"The shift from chromium trioxide to Cr(III) is possible but cannot simply be performed by changing the electrolyte. Cr(III)-based plating is very sensitive to impurities. Even small deviations in the process conditions can strongly influence the deposition success and the coating quality. Besides, Cr(III) electrolyte baths lasts much less than conventional baths (with Cr(VI))".* The shift is easy and simple as the same plating infrastucture can be applied. Only chemicals must be changed and toxic lead anodes must be replaced by graphite or MMO titanium ones. All other auxilliary like rectifiers can be the same.The evidence from Tecnocrom TripleHard® use (5 years of industrial use) and our own pilot industrial site use has demonstrated that the baths last as long as with traditional Chromium Trioxide.

The first version of TripleHard® was tested in (2015-2018) by Husqvarna and the results showed a need for some further developments in order to comply with their performance criteria. The latest TripleHard® solution, which now has been successfully tested in other relevant applications/uses will be suitable for Husqvarna. Savroc has proposed to Husqvarna to test the new solution as we are convinced that all the performance criteria (see 5.3.1.2 of AoA) can be met. Our solution is not only meeting the performance of CrVI, but exceeding it. It is also a more cost-effective solution, which can be implemented within a period of 6 months including testing, adaptation and plating process adjustments.

Environmental impact

The TripleHard® method will reduce the harm to the environment in comparison to using CrVI.

Emissions to air will be cleaner and require less filtration and a normal ventilation is sufficient. Waste and waste water treatment are easier and the overall process and impact is similar to a chromium trivalent process. Nickel substances are only used when superior corrosion resistance is required, however, in these cases less nickel will be required than when a CrVI method is used.

Health Impact

The chemical substances in TripleHard® are a lot safer for workers than CrVI and none are classified as SVHCs and hence the impact should be very positive. As TripleHard® is based on CrIII, which is an essential micronutrient for living organisms, so exposure causes little to no concern from a health & safety, or environmental perspective. Cr(III) is not water soluble (and therefore not mobile in the environment), so it is not leached from wastes and does not contaminate water supplies.

Conclusion

Many alternative methods to use of CrVI produce good coatings but require large investments in infrastructure and other changes for the coating companies. Trivalent chromium has been considered by the plating industry as the most potential method due to its similarity with a Chromium Trioxide plating process. TripleHard® trivalent chromium is industrially proven with excellent mechanical properties. It is easy for hard chrome plating companies to take into use, as most of the equipment does not need to be changed. All the chemicals in TripleHard® technology are REACH approved, and the costs of electricity, air purification, waste management are lower than in CrVI process.

By using TripleHard® chromium process, Husqvarna will be able to substitute CrVI within a period of 12 months. Mechanical performance of TripleHard® is better than with Chromium Trioxide and overall costs will be comparable or lower.

References

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