

An Update of New Conversion Coating for the Automotive Industry

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ABSTRACT

Over the past 60 years, chemical companies have been supplying automotive manufacturers state-of-the-art zinc phosphate conversion coatings which, when applied properly to a metal surface promote excellent paint adhesion and corrosion resistance. Phosphate conversion coatings have undergone many transformations over the years. Now some of their essential components and byproducts are being more tightly regulated under new environmental guidelines. The metal pretreatment industry is now challenged with the task to replace the traditional zinc phosphate coating with the next generation product. This paper will examine the advantages of a new generation conversion coating based on zirconium oxide. The performance and process cost savings will be discussed. This technology has been advancing over the past several years, and in 2007 several successful commercial line trials with this new conversion coating were conducted. Results of these line trials will be shown and the future of this technology will be discussed.

INTRODUCTION

With all the work by Thomas Coslett in the early 1900's as well as a host of others, it was not until 1943 with the introduction of the Jernstadt salt, a solution of disodium phosphate containing titanium ahead of the zinc phosphating bath that the zinc phosphate process was born as we know it today. The use of this salt allowed for the faster development of a more highly refined zinc phosphate crystalline structure. Over the past 60 plus years this basic process has been refined through many significant contributions, but the principal chemistry and function have remained the same.¹

Today's pretreatment industry is reinventing itself and retracing many of the developmental steps it took back in 1943. New processes are being studied in laboratories around the globe with collaboration amongst

colleagues to bring a new process to market. Figure 1 depicts the historical development of pretreatment as it has evolved over the past 60 years with very little change during the first 40 years. Over the past 20 years the most significant change was the introduction of the tri-cationic zinc phosphate system, which is the standard system used today.

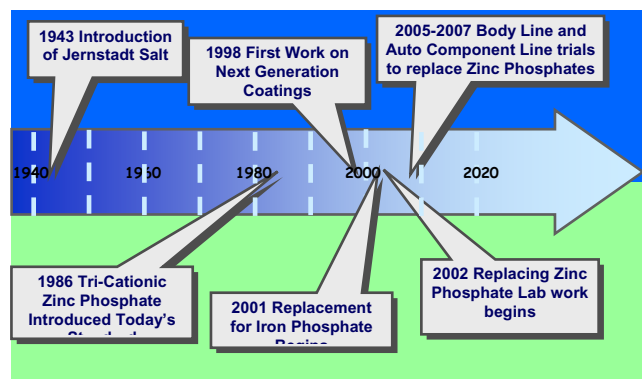


Figure 1

Over the past few years significant developments in metal pretreatment have allowed automotive manufacturers to begin to move away from the traditional tri-cationic pretreatment. These are significant game changing technologies that allow the manufacturers to save significant operational costs in the areas of energy, water consumption, sludge disposal and waste water treatment without sacrificing acceptable corrosion resistance or paint adhesion.

Suppliers are also seeing changes on the horizon driven by rising raw material and energy costs. With these rising costs, as well as ever-changing environmental regulations, suppliers are faced with tough challenges on how to change in order to maintain today's quality requirements in paint adhesion and corrosion resistance. Environmental regulations have played a significant role in the pretreatment process over the past decade and will continue play an ever-increasing role in the future. Environmental restrictions along with the impact of raw

material and energy costs are forcing the emergence of the next generation of pretreatment chemistries. As seen in Figure 2, the movement toward commercialization began in 2005 and has advanced to the point that successful automotive assembly line trials are now in progress. Once the new pretreatment process is verified as being production capable and the performance under real life conditions meets expectations it is likely just a matter of time before the industry is converted to these new technologies and a whole new process becomes the standard.

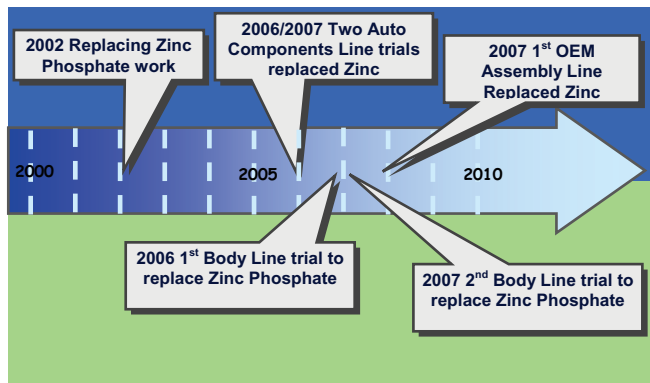


Figure 2

With increasing pressure from tightened environmental regulations to limit phosphate and heavy metal discharge, new conversion coatings need to be developed. The two metal ions, zinc and nickel, along with phosphate have been the backbone of the phosphate process for the last 60 years. Environmental regulations as well as increasing prices for nickel and zinc are the driving factors to develop suitable replacements. Nanoparticles, zirconium, titanium, polymers and additional metal ions, either by themselves or in combination, have been evaluated in the laboratory. The new conversion coatings are free of phosphate and any of the traditional heavy or regulated metals, Zn, Ni, and Mn, shorter than the current zinc phosphate process, and save energy and water costs, while offering the potential to meet the performance requirements of today's finishing industry. Coating weights can vary from supplier to supplier, but overall they are much less than a traditional zinc phosphate with a range anywhere from 20-200 mg/m² depending on the chemistry, substrate, and the application time. This compares to zinc phosphate coating weights that are 10-200 times higher! Lower coating weights mean thinner coatings, which helps explain the shorter processing times.

In some applications, the new generation conversion coatings meet all of the requirements mandated by customer specifications, while in others they meet most specifications. When the new generation pretreatments are compared directly to traditional zinc phosphate coatings, they often perform within current specifications, but perhaps at a lower level within certain corrosion specification limits.

New Generation Conversion Coatings Properties:

The coating formed by the new generation conversion coating process is significantly different from the standard zinc phosphate coating. The new generation conversion coating discussed here is composed of amorphous ZrO₂ rather than polycrystalline Zn₃(PO₃)₂. Figure 3 shows an X-ray Photoelectron Spectrum (XPS) of the new generation conversion coating on galvanized steel.

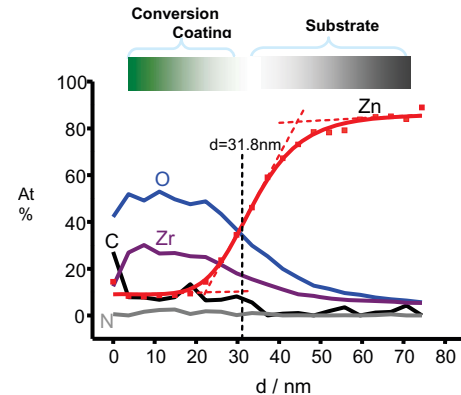


Figure 3

The XPS spectrum indicates that the new generation conversion coating on zinc surface is approximately 30-35 nm in thickness and composed primarily ZrO₂.

Coating Weight

In addition to the composition differences new generation coatings are significantly thinner compared to a zinc phosphate coating. Figure 4, shows the dimensional scale of various conversion coatings. The new generation coatings are generally less than 50 nm in thickness, which represents the thinnest coating among chromate, iron phosphate, and zinc phosphate.

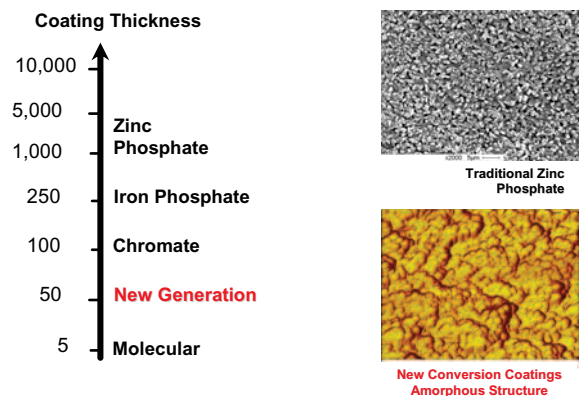


Figure 4

Appearance

Depending on the chemical make-up of the bath, typical coating weights range from 20-200 mg/m². Figure 4 show the amorphous structure on the cold rolled steel surface, as seen by Atomic Force Microscopy (AFM). Note that the scale on the AFM image spans just 1 micron across. The deposition rate for the new generation is very rapid, producing a complete coating within

approximately 20 seconds. At this rate of deposition, the overall manufacturing line could be reduced, thus freeing up additional manufacturing floor space. On the other hand, a zinc phosphate coating requires a minimum of 60 seconds deposition, is extremely thick in comparison with coating weights ranging from 1.5 – 4.0 g/m², and has a defined crystalline structure from 2 – 15 microns. By comparison, the zinc phosphate scanning electron micrograph (SEM) shown in Figure 4 is 50 microns across. The visual appearance of the zirconium oxide type coatings varies in color and is substrate dependent. The conversion coating color ranges from a golden iridescence on cold rolled steel, a bluish/grey on electro- or hot-dipped galvanized, and a near colorless appearance on aluminum. Regardless of the new conversion coating color, it is exceedingly hydrophilic, meaning that it holds a water layer very strongly, and this tightly held water sheath makes the treated surfaces very easily differentiated from untreated surfaces. Likewise, the coating color seems to have no effect on its performance.

Performance

The primary measurement of any new pretreatment is overall performance. Corrosion and adhesion performance with any conversion coating depends on three factors, the substrate, the pretreatment, and the paint system. The factors must work as one to meet today's corrosion and adhesion specifications. Depending on the specification and its ranges, the new generation coatings are capable of meeting specification requirements that were written for zinc phosphate. That means in many cases both processes are below the specification limits with regard to adhesion and corrosion, and hence they can be considered equal. Traditional zinc phosphate may perform slightly better within the specification range than the zirconium oxide coating. However, if both coatings meet the current specifications, the new generation coatings should see rapid commercial acceptance, considering the tremendous benefits of reduced energy requirements, waste water treatment, water usage, and manpower.

Status

In 2005, a paper was presented at SURCAR outlining the next steps in replacing the traditional zinc phosphate process.⁴ The presentation detailed development targets and the problems that each target was attempting to solve. The two major targets of the study were first to make the system environmentally friendly and second to reduce costs. Based on what we know today, the objectives outlined in the paper of reducing energy, waste water treatment, water usage, and manpower can be achieved with the introduction of these new conversion coatings. There are currently three automotive components lines on three different continents successfully running the new conversion coating process. There have been three short-run body trials since the 2007 SAE conference and each has been successful, i.e. sufficiently meeting the OEM expectations to the point that full production line trials are underway or in the final planning stages.

Short-Run Production Trial Results: Test Conditions

Two major domestic automotive manufacturers have conducted short-run production trials in 2007 to evaluate converting to the new conversion coatings in the day-to-day operations. In each trial, the existing pretreatment lines were used without modification and those pretreatment stages are summarized in Table 1 below. As seen in the table, a Greenfield system will require fewer stages than a traditional zinc phosphate washer, so considerable cost savings in installation and operation can be realized. It should be noted that the existing zinc phosphate lines were not optimally designed for the new conversion coating, but it was possible to use them without modification.

Table 1

Table 1					
Stage	Brownfield Configurations				Greenfield Considerations
	Trial 1		Trial 2		
	ZnPhos.	NGC	ZnPhos	NGC	
1	Clean *	Clean *	Clean *	Clean *	Clean *
2	WR *	WR *	WR	WR	WR *
3	S.Cond	WR *	S. Cond	WR	NGC
4	ZnPhos	WR *	ZnPhos	WR	RDIW*
5	WR *	WR *	WR	NGC	DIW
6	P.Treat	NGC	P.Treat	WR	
7	RDIW*	RDIW*	RDIW*	RDIW*	
8	DIW	DIW	DIW	DIW	

Note: * Indicated multiple stages
W. Rinse means tap water rinse
NGC is the new generation coating

In these trials, both vehicles and test panels were run. The panel substrates represented the metal mix of the vehicle, which included cold rolled steel, electro and hot dipped galvanized, galvalume and three aluminum alloys, 6111, 6016 and 6022.

Fully assembled vehicles were sent to their respective proving grounds for evaluation. Additional bodies along with test panels were run through the complete paint system together with a zinc phosphate control, then sent to the laboratory for evaluation. The fully painted vehicles were cut into test panels and evaluated along with the laboratory prepared and line processed panels. The vehicle and test panels were subjected to the required tests according to each automotive manufacturer's specification, which included GM 9540P and the Volvo VICT 1027, 149. With the market now being global the German standard cyclic corrosion test, VDA 621-415 was included in the evaluation. Besides the cyclic corrosion tests the proving grounds results will also be discussed.