Chemical pretreatment of continuous galvanized steel sheet in the automotive industry

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Since several years, new products appeared on the market replacing classic phosphate – based conversion coatings. This presentation will focus on the replacement of tricationic zinc phosphating systems for the automotive industry. The basic chemistry and coating properties are presented.
In the second part of the presentation, an outlook will be given on anti-corrosion packages for the coming decade. An example of a very lean automotive paint shop will be discussed.

Keywords: Phosphating, thin film pretreatment, zirconium oxide coating, direct to metal primer, multi metal car body, lean paint shop, process cost savings, waste water impact

INTRODUCTION

Zinc Phosphating, in combination with cathodic electro deposited primers, is since many decades state of the art in metal corrosion protection prior to painting. Over the last 20 years, only minor incremental improvements could be implemented, as the technology is quite mature.
Increased economical and ecological pressure arose over the last years to reduce the environmental impact of corrosion protection systems. In an automotive plant, e.g., the pretreatment system is the biggest consumer of process water, and it produces the highest amount of waste water. Nickel salts are considered to be carcinogenic, and employers are more and more concerned about health and safety issues of their employees. Cost pressure is not new to this business. Toyota was the first car manufacturer translating the shortcomings of the existing corrosion protection process into a two step vision of how the future of pretreatment in the automotive industry should look like [1, 2]. All these factors led to the development of a zinc phosphating successor system. Development targets were: Meeting OEM quality specifications, whilst minimizing process cost and reducing the ecological impact of metal pretreatment significantly.

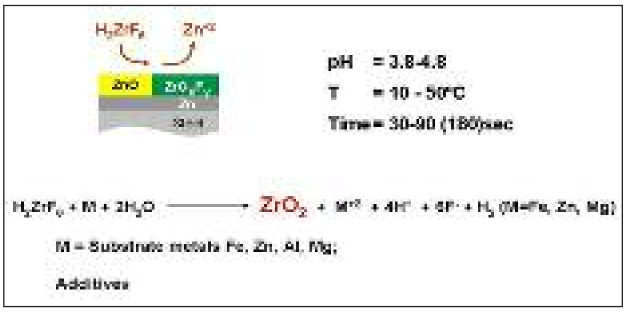

FIG. 1 ***Simplified conversion coating formation mechanism.***

Meccanismo semplificato di formazione del rivestimento di conversione.

CHEMICAL AND PHYSICAL PROPERTIES OF THE NEW PRETREATMENT SYSTEM

10 years of intensive research were necessary to finally come up with a new conversion coating system based on zirconium, fluoride ions and special additives.

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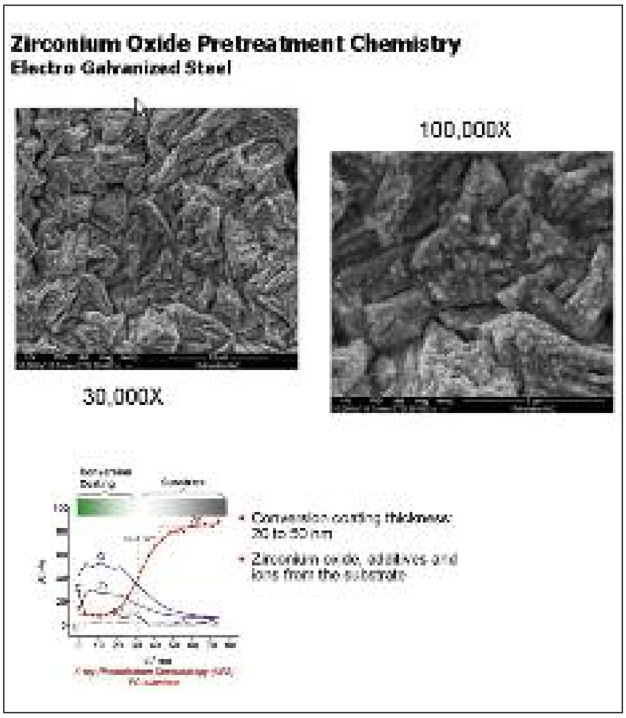

FIG. 2 ***Typical coating composition and film thickness (XPS, bottom), and FE-SEM micrographs (top) of a zirconium oxide coating.***

Composizione tipica di rivestimento e spessore del film (XPS, in basso) e migrografie FE-SEM (in alto) di un rivestimento a base di ossido di zirconio.

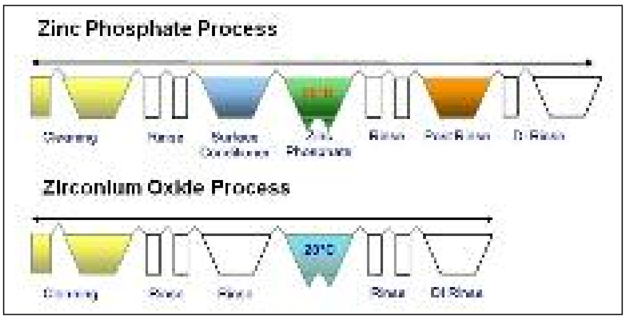

FIG. 3 ***Comparison of a traditional Zinc Phosphating process sequence to the much shorter zirconium oxide type o conversion coating.***

Confronto fra una sequenza di tradizionale processo di Fosfatazione con Zinco e una sequenza molto più breve per la tipologia di rivestimento a base di ossido di zirconio di conversione.

A ceramic type of coating is formed, typically in the range of 20 to 50 nanometers film thickness, consisting mainly of zirconium oxide, substrate metal ions, traces of fluoride, and a significant amount of performance driving additives [3, 4].

PROCESS CHARACTERISTICS

The new conversion coating system does not need any surface conditioner or accelerator any more, neither is a post rinse needed. This reduces the metal pretreatment line length significantly and leads to high savings in Greenfield lines. But even in Brownfield, existing lines, savings can be generated by shutting down not needed stages, or by reducing overall water consumption through cascading, the conversion of not any more needed stages into rinse stages [5].

As the new conversion coating system runs at much lower conductivities than a zinc phosphating system, less rinse water is needed to reduce the conductivity down to a level acceptable for subsequent electro coating applications. On top of that several customers are re-using the rinse water after thin film pretreatment as rinse water after cleaning, cutting thereby their overall water consumption at least in half. As a consequence, a maximum of 50 % of waste water, compared to a traditional zinc phosphating process, is generated. As the zirconium based pretreatment systems are free of phosphate, further savings occur in waste water treatment. No Phosphate from conversion coating, no Nickel has to be eliminated, much less waste water treatment sludge is generated.

In times of high cost for energy, users are especially fond of the fact, that thin film pretreatment does not need any heating. On top of that, the process has a much lower etch attach to the base metal. This fact leads to a higher focus on the cleaning and degreasing part of the metal pretreatment process, as metal oxides have to be removed in the cleaner stage. On the other hand, maximum 10 % of the amount of sludge, created in a zinc phosphating process, will be formed with this new technology. The sludge consists of iron oxide, which is much less sticky. Reduced maintenance for nozzle cleaning, de-sludging and overall maintenance are the results. Some customers have in the meantime shut down their de-sludging system completely. For new to be constructed plants, investments for de-sludging and heating can be saved. On line analysis is easy and fast. Just the need for X-ray fluorescence as analytical tool for coating weight determination is more complicated than for a zinc phosphating process.

LINE CONVERSION RESULTS

The first line trials with the new system were carried out in 2006

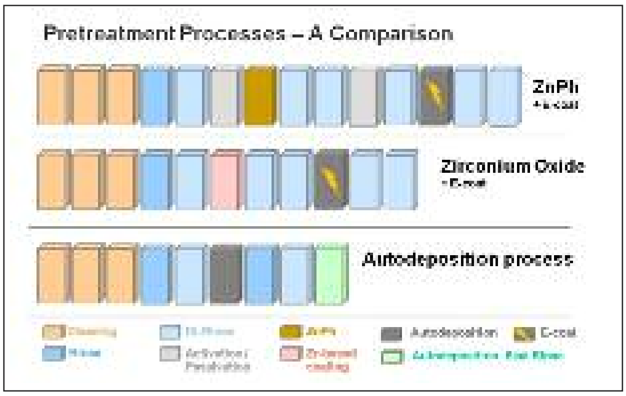

FIG. 4 ***Comparison of a standard Phosphating- and e-coat process (top), as in use today, with a zirconium oxide pretreatment in combination with e-coat (middle) and the future combined corrosion protection process (bottom).***

Confronto fra un processo standard di Fosfatazione e di e-coat (sopra) attualmente utilizzato, e un pretrattamento con ossido di zirconio abbinato ad un trattamento e-coat (al centro) e il futuro processo combinato di protezione dalla corrosione (sotto).

after extensive preparation via panel programs and in close cooperation with E-coat companies.

The system was very easy to start-up, and much to the surprise of all parties involved, it was very easy to be maintained. This led very soon to automotive body line conversions in 2007.

The system was fast and easy to be started up, no appearance problems occurred. These findings were repeated now in many other automotive body lines and automotive supplier lines all over the world. The anticipated water- and energy savings were confirmed, maintenance schedules drastically reduced, stages and pumps taken out of the pretreatment system.

The corrosion protection and paint adhesion of a standard tricationic zinc phosphating system and the new thin film – or zirconium oxide based pretreatment are, depending on the type of test performed, on a comparable level. Even throw power, although depending on the e-coat system in use, is very much comparable for zinc phosphating and the new, zirconium based system.

PERFORMANCE TODAY AND NEXT STEPS

Having now a vast knowledge of the new system, active in many lines, tested according to a big number of automotive and non-automotive specifications, in combination with a wide variety of e-coat and powder coat system, we can say today that the new zirconium based system performs in average very much comparable to zinc phosphate. However, we can not neglect the fact that generations of e-coat and powder coat were developed for zinc phosphated substrates. This leads to the fact, that zinc phosphate, if run in its very narrow specification limit concerning the many control parameters to be observed, in some cases still performs slightly better than the new system.

Teams of chemists all over the world are busy right now to boost the performance level of the new technology even higher, and intermediate results so far are very promising. New additives are improving both corrosion- and adhesion performance.

OUTLOOK PAINTSHOP 2020

Zirconium Oxide based conversion coatings will only be a bridge technology into the near future. Water consumption for paint booth air balancing, energy consumption for multiple ovens will

FIG. 5 ***Tata ACE truck paint shop lay-out. The leanest automotive paint shop operating today.***

Schema dell'impianto di verniciatura della Tata ACE, che è più semplice attualmente operante.

put a growing cost burden on all metal painting operations. This is why several OEMs developed their 2015 – 2020 paint shop strategies [1,2]. One of the elements of these strategies is the combination of today's functionalities of pretreatment and e-coat into one new technological step, as Figure 4 explains.
The replacement system, auto-deposited paint and pretreatment substitute in one step, has to take over all corrosion protection properties of its technological predecessors. Electro - less deposition on clean surfaces will make "throw power" a forgotten word in the future. Less holes for ensuring enough coating film thickness on interior parts will allow more rigid and more light weight car body constructions. The main challenge of such systems will be the combination of superior edge protection and paint film appearance. Autodeposition, at least, will not depend on electromagnetic field density distributions concentrated at sharp edges.
This sounds like a very futuristic scenario, but it was put in place already in 2007 for the Tata ACE light truck in India. Tata has the strategy to build very lean paint shops in the future, as explained during the 2008 Berlin strategy conference [6].
The autophoretically applied anti-corrosion primer is applied, then just de-watered, and not cured. In a so called co cure process, powder paint is applied on the dry to touch grey autophoretic paint film, then both paints are cured together in the single paint oven in this plant.
Concepts like this are allowing to build new paint shops in a very short amount of time, on minimum space requirements, with minimum invest and process cost. Concepts like this will change the world of automotive paint shops are all of us were used to deal with over the last decades.

SUMMARY

The substrate mix of modern and future car bodies will become more and more complex, with weight saving as main target. Zinc Phosphate- and cathodic e-coat technologies, introduced in the second half of the last century, will be replaced in two steps.
First, the current zinc phosphate process will be replaced, with or without intermediate steps like the two-step process [7], by a low ecological impact thin film pretreatment technology. Step two will be a combination of today's zinc Phosphating and e-coating process in one process step, as auto- or electro deposited direct-to-metal technology. And the future already started in 2007!

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Abstract

Pretrattamento chimico di lamiera di acciaio zincato in continuo nel settore automotive

Parole chiave:

Da diversi anni, sono apparsi sul mercato nuovi prodotti che hanno sostituito i classico rivestimenti di conversione a base di fosfato. Questa presentazione si concentra sulla sostituzione dei sistemi di fosfatazione ai sali di zinco tricationici nell'industria automobilistica. Vengono presentate le proprietà di base chimiche e di rivestimento.
Nella seconda parte della presentazione, verrà fornita una previsione sui pacchetti anti-corrosione impiegabili nel prossimo decennio. Sarà analizzato un esempio di impianto di verniciatura nel settore automobilistico.