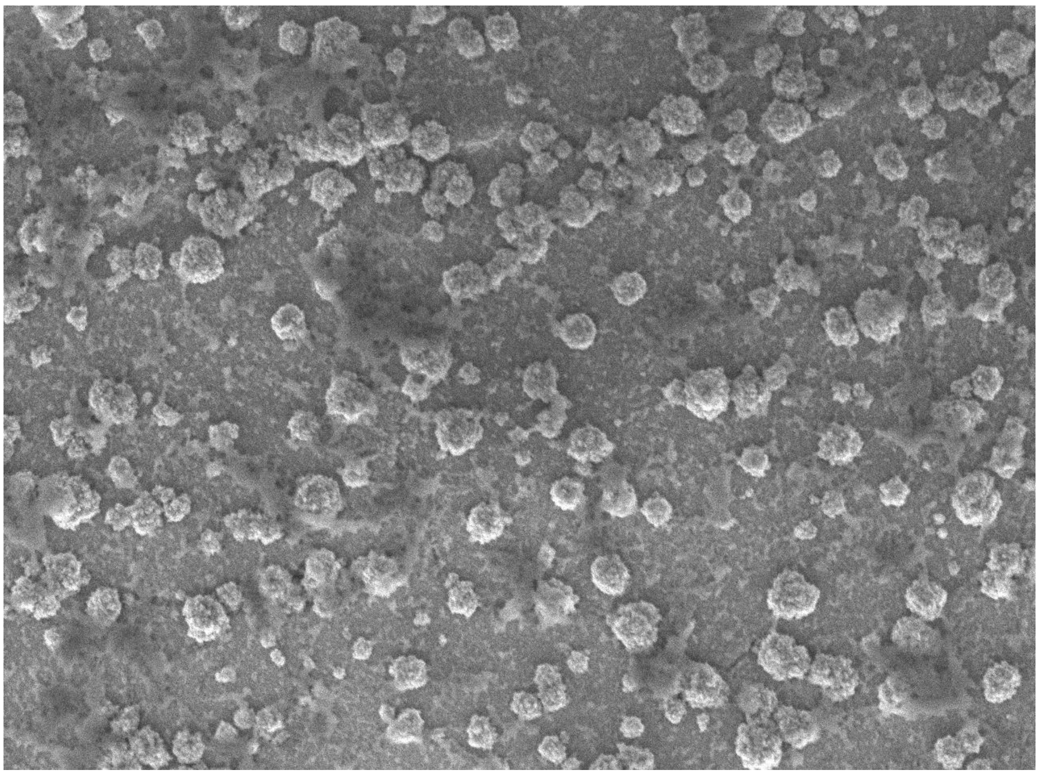
ECOSUS - Ecologically Sustainable Pretreatments for Painting Multimetal

Public report



Project within Sustainable Manufacturing Systems

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Content

1. Summary

Environmental regulations are becoming more demanding and have large impact on the industry today. During vehicle production the paint shop (including cleaning, pretreatment and painting) is one of the units with highest water-, chemical- and energy consumptions. During the last decade large efforts have been done to find an alternative for zinc phosphating since this pretreatment process consume large amounts of water and energy, it produce high amount of sludge as well as it contains heavy metals where nickel is of most concern. Another drawback with this process is that it is limited to 10-20 % of aluminium in the pretreatment bath.

The project had the following objectives:
1. *A developed/optimized thin film process/product that gives a corrosion protection as good as ZnPh.* Systematic studies correlating process parameters – film structure/composition - corrosion protection will be done. Process/product development will be performed by chemical suppliers cooperating with the project team.
2. *Predict the long term performance of thin film coatings*. Correlation of accelerated test methods that degrade the surface coating and field test will be defined.
3. *Introduce thin film technology at a paint shop/subcontractor treating one/few substrates*.
4. *Investigate an alternative pretreatment*, Nickel-free ZnPh as it is another possible step to take in order to minimize the use of toxic substances in the surface treatment.

The project has been divided into different panel applications where the two first had the focus on process variations, corrosion performance and coating composition. Within the first panel applications also the long term performance of the coatings has been investigated where accelerated test methods as well as field exposure has been evaluated

The third panel application investigated how the cleanliness, wash methods and different oils (both new applied and aged) affects the corrosion performance as well as the adhesion between paint and substrate.

Substrates investigated for all panel applications have benn cold rolled steel (CRS), hot dip galvanized steel (HDG) and hot rolled steel (HRS)

The results and outcome of the project has been:.

- A deeper understanding between process parameters and corrosion performance.
- A deeper knowledge of the coating composition and the influences on the corrosion performance.
- For HDG and HRS the corrosion performance are on the same level as for ZnPh but for CRS the thin film coating has still a larger paint delamination.
- Correlations between accelerated corrosion tests and field tests.

- Evaluation of methods for measuring the adhesion between the paint / coating / substrate.
- Evaluated methods for quality assurance of the coating.
- Line trials at Volvo AB, changing from ZnPh to thin film technology during one weekend.
- First step in evaluation of nickel-free ZnPh as an alternative to ZnPh with SEM, accelerated corrosion test and field test.
- Evaluations on how the cleanliness, washing methods and different oils influence the coating and the corrosion performance.

2. Sammanfattning på svenska

Lagar och reglementen kring kemikalier, energi och miljö blir allt mer omfattande och har idag en stor inverkan på industrin. Inom fordonsindustrin är ytbehandling (tvätt, förbehandling och lackering) en av processerna med den högsta vatten-, kemikalie- och energiförbrukning. Under det senaste årtiondet har mycket arbete lagts ned för att utveckla alternativ till zinkfosfatering, då denna förbehandlingsprocess förbrukar stora mängder vatten och energi, producerar en stor mängd slam såväl som att den innehåller tungmetaller och då specifikt nickel. En ytterligare nackdel med processen är att den har en begränsning till att behandla max 10-20% aluminium i förbehandlingsbadet på grund av den stora mängden slam som annars bildas.

Målen med projektet har varit:
1. En utvecklad/optimerad tunnfilmsprocess/-produkt som ger ett korrosionsskydd lika bra som ZnPh genom systematiska studier som korrelerar processparametrar till filmstruktur/komposition och korrosionsskydd. Samtidigt kommer kemileverantörerna att genomföra en viss process/produktutveckling.
2. Att kunna förutse den långsiktig prestanda av tunnfilmsbeläggningar. Korrelationen mellan accelererade testmetoder och fälttester är en viktig del.
3. Introducera tunnfilmsteknik hos en underleverantör som behandlar ett fåtal substrat.
4. Undersök en alternativ förbehandling, nickelfri ZnPh, detta ger en alternativ möjlighet för att minimera användningen av giftiga ämnen i ytbehandlingen.

Projektet har uppdelats i tre olika panelapplikationer där de två första har fokuserat på processvariationer, korrosionsprestanda och beläggningskomposition. Inom den första panelapplikationen har även beläggningarnas långsiktiga prestanda undersökts där förlängda accelererade provningar och fältexponering har utvärderats

Den tredje panelapplikationen undersökte hur renhet, tvättmetoder och olika oljor (både nyapplicerade och åldrade) påverkar korrosionsprestandan såväl som vidhäftningen mellan färg och substrat.

Underlag som undersökts för alla panelapplikationer har varit kallvalsat stål (CRS), varmförzinkat stål (HDG) och varmvalsat stål (HRS).

Resultat inom av projektet har varit bland annat

- Djupare förståelse mellan processparametrar och korrosionsprestanda.
- Fördjupad kunskap hur processparametrar påverkar beläggningskompositionen och hur den i sin tur påverkar korrosionsprestanda.
- För HDG och HRS är korrosionen på samma nivå som för ZnPh men för CRS har tunnfilmsbeläggningen fortfarande ett större korrosionsutfall.
- Korrelationen mellan accelererade korrosionstest (6, 12 och 18 veckor) och fältprovningar (1,2 och 3 år). Fältprovningar efter 3 år har överlag haft en lägre korrosionsutbredning än accelererade korrosionsprovningar efter 6 veckor. Båda metoderna har uppvisat en linjär ökning i utbredning under provtiden.
- Utvärdering av metoder för mätning av vidhäftning mellan färg / beläggning / substrat.
- Utvärderade verifieringsmetoder för kvalitetssäkring av beläggningen såsom bland annat SEM och XRF.
- Linekörningar hos Volvo Tuve där byte gjordes från ZnPh till tunnfilmsteknik under en helg. Tunnfilmsförbehandlingarna uppvisade inte samma korrosionsprestanda som ZnPh. Korrosionsprestandan kunde höjas ytterligare genom att använda ett 2-skikts färgsystem. Innan linekörningen visade det sig att det var svårt att rengöra systemet innan påfyllnad av den nya förbehandlingskemin (tunnfilmsförbehandling) skedde.
- Första steget i utvärderingen av nickelfri ZnPh som ett alternativ till ZnPh, utvärderat med SEM, accelererat korrosionstest och fälttest. Den Ni-fria ZnPh uppvisade en likvärdig korrosionsprestanda som ZnPh men ytterligare verifieringar kan behövas.
- Utvärderingar av hur rengöring, tvättmetoder och olika oljor påverkar beläggningen och korrosionsprestanda. Tvättprocess och olja påverkar inte korrosionsskyddet nämnvärt så länge ytan blir tillräckligt ren. Finns däremot kontamineringar kvar på ytan så kan korrosionen öka markant.

3. Background

Environmental regulations are becoming more demanding and have large impact on the industry today. Automotive industry is working actively to reduce environmental impact by for example using lighter structures to allow lower energy consumption while driving, use sustainable materials and to lower usage of hazardous chemicals. During vehicle production the paint shop is one of the units with highest water-, chemical- and energy consumptions. The paint shop includes cleaning steps, pretreatment process and painting.

During the last decade large efforts have been done to find an alternative for zinc phosphating since this pretreatment process consume large amounts of water and energy, it produce high amount of sludge as well as it contains heavy metals where nickel is of most concern. Another drawback with this process is that it is limited to 10-20% of aluminium in the pretreatment bath. This will become a problem since the amount of aluminium in the car body is growing as an effect of the light weight concept.
The role of zinc phosphating as a pretreatment method is to secure good corrosion resistance. Zinc phosphate crystals are deposited as a layer with a thickness of typically a few micrometers. Corrosion resistance of a layer of zinc phosphate together with automotive paint systems is good and well documented as well as the process is stable, resulting in good quality. It will be a challenge to find a candidate system that can provide the same quality in terms of long term corrosion resistance.
One of the most promising alternatives to zinc phosphating is “thin-film technology” relaying on conversion coatings forming a thin transparent films by interfacial precipitation of metal oxides/hydroxides from the base material mixed with precipitates of hydrated ZrO_2. The metal oxides are combined with additives such as silica particles, silanes, organic additives and species that promote paint adhesion and copper to improve film formation. These coatings can be used for both single material and multi-material applications. The coating formation, composition and corrosion properties have studied for aluminum alloys, magnesium alloys, zinc coated steel (including Zn-Al coatings) and carbon steel. Thin-film technology has a lower environmental impact than zinc phosphating allowing less energy- and water consumption as well as it do not contains heavy metals and sludge formation is reduced.

4. Purpose, research questions and method

Thin film technology has until today showed promising results from an environmental as well as a technical point of view but still deeper knowledge is necessary before the new technology can be implemented regarding for example process variations, long term performance, validation between accelerated corrosion tests and long term field tests as well as how process variations influences changes in the coating composition.

Within the project three panel applications have been performed and evaluated. The choice of material; substrates (hot rolled steel, cold rolled steel and hot dipped galvanized steel) and paint material for the three panel applications has been decided within the project consortium.

Before each panel application the project consortium have had discussions together with the chemical suppliers in order to identify and set the interested parameters and to confirm the set-up of each application. Also, the suppliers have informed the project group regarding the development within the area.

The two first panel applications had a focus on process variations as for example; bath concentrations, treatment time and application methods and to correlate these variations to:

- Coating morphology.
- Corrosion performance through accelerated corrosions tests.
- Long term corrosion tests through extended accelerated corrosion tests and field tests on trucks.
- Coating composition / concentration in XY-plane and in Z-led.
- Barrier properties through electro chemical investigations.

The second panel application is based on results from the first panel application.

The third panel application had focus on:

- How the cleanliness of the surface influences the corrosions performance.
- How the cleanliness of the surface depends on different kind of oils, newly applied or aged, and different washing methods, dip or spray + dip, affects the degree of cleanliness.

In addition to the three panel applications line trials have been performed at Volvo Trucks in order to evaluate the performance of the coating in a production line.

5. Objective

The corrosion protection of thin-film pretreatments has been shown to be inferior to zinc phosphate in some cases, especially when applied on steel. Further process/product development and especially studies correlating the pretreatment film composition and the corrosion performance are necessary as well as prediction of the long term performance.

The project had the following objectives:

1. *A developed/optimized NPT process/product that gives a corrosion protection as good as ZnPh.* Systematic studies correlating process parameters – film structure/composition - corrosion protection will be done. Process/product development will be performed by chemical suppliers cooperating with the project team.
2. *Predict the long term performance of NPT.* Correlation of accelerated test methods that degrade the surface coating and field test will be defined.
3. *Introduce NPT at a paint shop/subcontractor treating one/few substrates.* This is an important step to take measures for reduction of the environmental impact of surface treatment. It will also increase the industrial experience of NPT.
4. *Introduce Nickel-free ZnPh at a subcontractor.* This is another possible step to take in order to minimize the use of toxic substances in the surface treatment.

A “best practice” of running thin-film pretreatments on a steel substrate will be delivered. The project will deliver data concerning the long term performance of thin-film pretreatments. Another important delivery is a model for predicting corrosion in order to forecast the corrosion properties of products from the process conditions. The project is expected to deliver data, experience and instructions so that a nickel-free ZnPh process safely can be introduced in any paint shop

6. Results and deliverables

The main goal of the project is directed towards the program target for Sustainable manufacturing, the contribution to the program goal to reduce the environmental impact of the manufacturing processes with 30 %. By changing the pretreatment process from ZnPh to thin film pretreatments the energy consumption can be reduced with as much as 30 % and the global warming potential by 35 %. Within the environmental program a central part is to develop techniques for a decreased environmental impact for surface treatment processes. This project is one important step to speed up the implementation of new technology both within the automotive industry as well as for other manufacturing industries.

A change from ZnPh to thin film coatings can reduce the amount of sludge for destruction with at least 80 %. This is an environmental as well as a cost reducing factor that can increase the competitiveness for the Swedish industry. Also the physical area needed for the surface treatment process can be reduced as the process line for thin film pretreatments is shorter (a lower number of process baths) than for ZnPh.

The results from the project is of high interest for both the Swedish automotive industry as well as the Swedish industry and results from the project. There are a large amount of SME:s both in-house coaters as well as job coaters searching for alternatives in order to have an easier, cheaper and more environmental acceptable process for whom the result of the project are of great importance.

Introduction of a Ni-free ZnPh or a thin film pretreatment process at a job-coater, supplier or automotive company have not been a great topic during the project time.

One line test at AB Volvo has been performed during the project. Panel preparations, painting and evaluations from an existing thin film pretreatment line at QPC have been one part of the project as well.

More specific results delivered from the project are following:

- The paint delamination of samples pretreated with thin film pretreatments was similar or slightly higher compared to phosphated samples after cyclic corrosion testing (ACT-I). This is valid for all materials tested, HDG, CRS and HRS.
- After field exposure, the delamination of samples pretreated with the thin film technology was similar to phosphated samples for all tested materials, HDG, CRS and HRS
- The extended paint delamination ACT-1 (18 weeks) vs field (3 years)
    - HDG material after ACT-I was approximately 3 times higher compared to field exposed samples

    - HRS material after ACT-I was approximately 2 times higher compared to field exposed samples

Analysis of the pretreatment films:

- Process parameters such as treatment time and Zr content affect the composition, structure, thickness and electrochemical properties of the pretreatment layers. The coating weight (amount of Zr) is strongly influenced by the treatment time and the Zr content of the bath.
- The substrate influence the formation of the pretreatment layers and thinner films are generally found on the CRS substrates. On HDG the formation of hydrated Zr-oxide is promoted and layers with higher coatings weights (mg Zr / m^2) are observed
- Paint delamination for CRS is affected by the film composition and structure (influenced by the process parameters). It was observed that the highest coating weights are not beneficial for the paint delamination (although very low coating weights should be avoided)

It is suggested that the pretreatment layers influence the paint delamination rate only indirectly, for instance by improving the paint adhesion.

- This explains the small effects observed of the pretreatment composition on the paint delamination observed for HDG for which the paint delamination is controlled by the anodic undermining (anode in the delamination front) of the zinc layer.
- For CRS the paint delamination mechanism is probably also anodic but due to formation of voluminous corrosion products under the paint film mechanical stresses in the paint film are induced and promote paint delamination.
- Stabilisation of the paint / substrate interface and paint adhesion is therefore more important compared to HDG were the corrosion products are less voluminous.
- The lower paint delamination rates observed for HRS is probably related to improved paint adhesion by mechanical interlocking of the paint to the substrate.

7. Dissemination and publications

7.1 Dissemination

How are the project results planned to be used and disseminated?	Mark with X	Comment
Increase knowledge in the field	X	The project has increased the knowledge regarding process parameters, corrosion mechanisms both for accelerated corrosion as well as for field test, importance of cleanliness
Be passed on to other advanced technological development projects	X	The industry is still interesting in the technology as a complement to ZnPh and the project has resulted in a deeper understanding useful for industrial implementation.
Be passed on to product development projects		
Introduced on the market		
Used in investigations / regulatory / licensing / political decisions		

The most important drivers of change for the automotive industry are due to changes in the chemical regulations or other laws or regulations. Another parameter with very high impact is the corrosion performance of the coatings, as long as the corrosion performance is not as high for a new pretreatment as for the one used today the driving force for changes is rather low as long as there are no other driving forces for changes. Other important factors for changes can be for example lack of phosphorus which is one of the components in ZnPh or restrictions of the water usage due to shortage of water.

Other important driving forces are increased customer awareness that increase the need for environmental declarations of products as well as for the production processes and used material. The surface treatment process will have a great influence on the environmental impact on the production process both from a process view i.e. high energy consumptions, high water usage, huge amount of sludge formation as well as from a component view as for example nickel.

Also, changes of the infrastructure that can have an impact on the production process is when the ownership of cars goes from private owned to car pools due to environmental and sustainability reasons.

External projects that can have a great impact on the dissemination of the results are new exploitation or renovation of surface treatment lines when new technology can be implemented. The line for thin film treatment is not consuming as much production area as ZnPh as the lines are shorter with a less number of process steps. Another driving force is if other automotive companies abroad convert to thin film pretreatments showing a high corrosion performance as well as other advantages and serve as a pattern.

7.2 Publications

Klusterkonferens, 2016, 2017
Ytskydd 2015, 2016
Goda exempel , Swerea, 2016
Corrosion News, 2016
Teknik och Tillväxt, 2016
Scandinavian Coating, 2017
Automotive Painting, 2017
Ytforum, 2017
Eurocorr 2017

8. Conclusions and future research

Even if the project has shown similarity in corrosion performance between ZnPh and thin film coatings and a process window that do not show large variations of the corrosion performance, the automotive companies are reluctant to convert from the surface treatment process of today, ZnPh, to thin film technology. Even if it has been shown during this project and earlier projects as well that the thin film technology has a lot of environmentally and economically advantages as for example low amount of sludge formation, lower process temperatures, lower water consumption and lower costs there are still a number of uncertainties when converting from one system to another one where some topics interesting for future research have been identified as:

- Methods for process verifications. SEM is not suitable as a verification method for characterization of the coatings. XRF is currently used as the method for measuring coating weight but is a rather rough / limited method and not suitable for coating coverage or quality assurance of the coatings.
- Another important topic within verification methods are the accelerated corrosion methods that are developed for ZnPh, are they suitable for thin film pretreatments? Accelerated Corrosion tests and field test are not direct correlated to each other but they show similar trends and corrosion mechanisms. Test methods to discriminate different pretreatments under worst-case scenarios need to be developed.

- Digitalization of the surface treatment process by multivariate methods in order to collect in-put data and extract information regarding the conditions of the process baths, concentrations, temperatures as another way for quality assurance of the coatings.
- Guidelines for surface treatments with thin film coatings.
- Quality assurance of in-coming material
- Multimaterial components, (joined components), how is the quality of the pretreatment affected by joining dissimilar materials (galvanic effects), how are the corrosion properties of pretreated and joined multimaterials, how are geometric constraints affecting the pretreatment quality (for instance crevices),and where the surface treatment should be located during the production.

9. Participating parties and contact persons

Company	Contact person
AB Volvo	Henrik Kloo, industrial project leader
Swerea IVF	Cecilia Groth, Project administrator
Volvo Car Corporation	Jörg Wohner
Scania CV	Annelie Önsten
Volvo Construction Equipment	George Stare
QPC	Christer Lundh
VBG-group	Erik Olsson
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