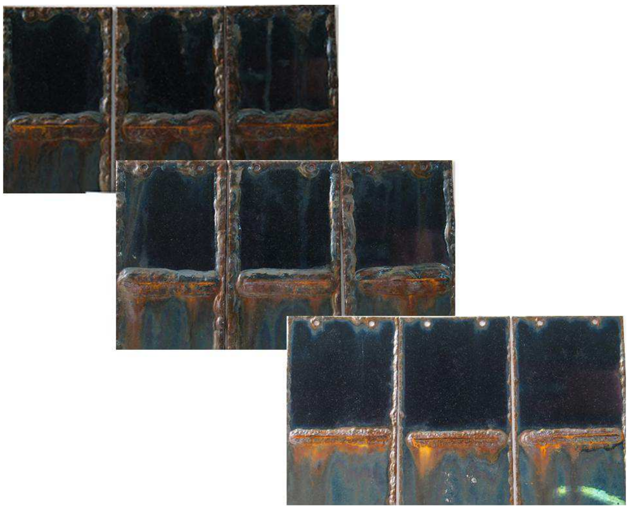
New pretreatment processes based on silanes a/o Zr/Ti for replacing zinc phosphating and zinc phosphating and ED-coating



Project within ***Sustainable Manufacturing Systems***

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Date 120606

Content

FFI in short

FFI is a partnership between the Swedish government and automotive industry for joint funding of research, innovation and development concentrating on Climate & Environment and Safety. FFI has R&D activities worth approx. €100 million per year, of which half is governmental funding. The background to the investment is that development within road transportation and Swedish automotive industry has big impact for growth. FFI will contribute to the following main goals: Reducing the environmental impact of transport, reducing the number killed and injured in traffic and Strengthening international competitiveness. Currently there are five collaboration programs: **Vehicle Development, Transport Efficiency, Vehicle and Traffic Safety, Energy & Environment and Sustainable Production Technology.**

For more information: www.vinnova.se/ffi

1. Executive summary

The overall objective of this project was to be able to substitute zinc phosphating as pretreatment system with new pretreatment system (NPT). The main reason being that:

- Zinc phosphating (ZnPh) is expensive to run due to the sensitivity to different alloys that require extensive supervision of a great number of parameters and steps.
- ZnPh generates a large amount of waste, due to sludge formation, particularly from aluminium surfaces and wastewater treatment of rinse water contaminated with process chemicals.
- The amount of aluminium is foreseen to increase within the next years due to the demands for lightweight cars and trucks.

The aim was to attain results, which would make it possible to shift to a new pre-treatment process at the OEMs within 5 years and at the first subcontractor within the time limit of this project.

It has been a horizontal project with Volvo Technology as the project leader. New surface treatment plants were planned to be built within the next years both at companies within the Volvo group and at subcontractors. The other industrial partners were Scania CV, Volvo Cars, SAAB Automobile and subcontractors. Academic partners were Swerea IVF and Swerea KIMAB.

The main objective was to establish within 5 years a reliable alternative to the present Zn/Mn-phosphating and ED-coating used by vehicle producers and major sub-suppliers. The purpose was to develop a new pre-treatment system (NPT) that:

- Is robust and allows coating of assembled parts from several materials.
- Gives the same quality versus corrosion and adhesion to the following coating system as to the system used today, with greater flexibility for multi material
- Means less disturbance, disposal products and energy cost.

The project started with a collection of data from evaluations or NPT performed by the project participants, as well as collection of requirements to be fulfilled by NPT systems. The standards defined by the OEMs were used as background for this work. As the standards are based on various analytical techniques or accelerated tests, it was necessary to find new analyses or verify the reliability of existing analyses/tests in order to obtain reliable data of NPT compared to ZnPh. The main effort of the project work has therefore been to analyse and test NPT systems.

The overall conclusion is that the new pretreatment systems give promising results on aluminium and galvanized steel but do not have a corrosion performance that reaches the *same level as zinc phosphate on steel* at least not on cold rolled steel. *There are still some doubts concerning the long term performance of NPT that has to be evaluated.*

Some other important results generated during the project are listed below:

- The processes for NPT are rather stable and have wide processing windows
- NPT systems can be generally introduced at subcontractors and OEM's without large investments. This was shown by trials at one of the OEMs during the project.
- Introduction of NPT means large savings of energy and water.
- ACT as an accelerated evaluation method shows good correlation to field test after 2 years of exposure. FTIR studies reveal the same type of corrosion products after accelerated and field test and similar corrosion mechanisms are suggested.
- Some characterization methods for NPT have been evaluated. Coating weight measurements by X-ray fluorescence (XRF) and micro structural studies by FEG-SEM give reliable significant results concerning the quality of the coating. These instruments are possible to use close to production (at least for OEMs).
- TEM studies give in-depth knowledge about the thickness and composition of the coatings.

2.Background

Today vehicles are assembled from many types of materials like steel, zinc, aluminium and magnesium and the strive for more light weight cars has contributed to an increase of for example aluminium. Also high strength steel is in use and stainless steel is on its way. There is a general focus on environmental improvements in the production of vehicles and it is therefore necessary to consider the surface treatment process as this includes the use of a lot of encironmentally hazardous chemicals, production of waste as well as a high consumption of energy and water.

The New Pretreatment Systems that have been commercially available for the last 5 years hold the promise of a considerable reduction of the use of chemicals, energy as well as a reduction in the amount of waste that is created. However, the performance of the corrosion protection has been very varying and there has been a lack of verification of the accelerated test results with field results. Replacing a well known surface treatment process includes a large risk that must be minimised by thorough studies of the properties. This has been performed in this project

3.Objective

An overall objective has been and still is to within 5 years establish a reliable alternative to the present Zn/Mn-phosphating used by vehicle producers and major sub-suppliers. In order to move in this direction several activities had to be performed such as:

- Describing requirements
- Finding reliable characterization methods, analyses and tests
- Studying process parameters and their correlation to performance
- Obtaining relevant procedures for evaluation and qualification of NPT systems
- Correlate data from accelerated test to field test
- Gain experience from introduction of NPT by trials and large scale evaluations

4.Project realization

The project has been performed with a close cooperation between the research performers (Swerea IVF and Swerea KIMAB) and the OEMs (Scania, Volvo Technology, Saab and Volvo Cars Corporation) as well as the participating subcontractors (Proton and Konga Bruk). The project realization can be described as follows:

- The steering committee with representatives from each participating company has planned and controlled the project and taken decisions at project meeting with all partners attending.

- Planning and performing experiments such as preparation of test panels have been performed by a joined effort with OEMs supplying material (substrate and paint), participating in pilot plant production and applying paint.

- The research partners have performed most of the analyses of NPT requiring equipment not used for evaluation of traditional zinc phosphating.

- An “Analysis Group” was formed with experts from the partners (OEMs, subcontractor and institutes) to receive, analyse and discuss the results when studying the NPT systems.

- Accelerated corrosion tests and field exposures have been performed by participating companies.

- Production trials of NPT have been performed by several of the partners (OEMs and subcontractor).

5. Results and deliverables

The deliverables as listed below were decided in the beginning of the project has been documented as reports or presentations throughout the project.

- Requirements specified for coating
- Description of methods for quality follow up
- Description of methods for process control
- Description of QA system at subcont. for new pre treatment proc.
- Report from screening and technical evaluation
- Eval. of cost, environm., LCA and optimised cleanliness
- Report on adaption, development and optimization of proc.
- Demonstration plant at one subcontr. or OEM
- Final report: results, demo plant and need for further work

5.1 Materials

The various substrates were provided by the participating vehicle manufacturers. Thus the following substrates were used in the evaluations:
Aluminium 6016, provided by Saab,
Galvanized steel - HDG, provided by VCC
Cold rolled steel – CRS provided by Volvo and Saab
Hot rolled steel – HRS, provided by Scania
(ZnMgAl, Scania)
(Usibor 1500, Scania)

The new pretreatments (NPT) that have been evaluated contain a zirconium component (H_2ZrF_6) that creates the possibility to form a protective oxide film on the metal substrate. NPT can also contain silane(s) and/or water soluble polymers. The evaluated systems have been designated “A” and “B” in some evaluations. Different treatment times and/or differences in chemistry gives designations such as “Xa” or Xb” where X is A or B. Various paint system, agreed by OEMs , were used. Details can be found in the project report

5.2 Results

Structure and compositions of the pretreatment film

Films/ Coatings of the new pretreatment systems have been studied by different techniques; FEG-SEM, FIB-SEM / TEM, FTIR, FTIR and XPS. The results show that the films have a thickness in the range 20-100 nm and consist of Zr-oxide/hydroxide with incorporated organic components, such as silanes or other organic species There are probably also elements (Al, Zn, Fe) from the substrate incorporated in the film.

FEG-SEM studies
Films/ Coatings of the new pretreatment systems have been studied by FEG-SEM on different substrates as shown in figures 1-6. Note that the images have different magnifications.

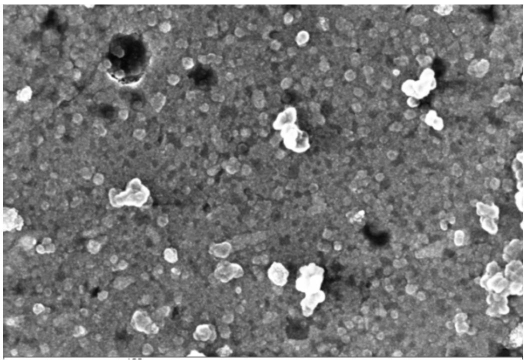


Figure 1. NPT on aluminium 6016,batch 1.

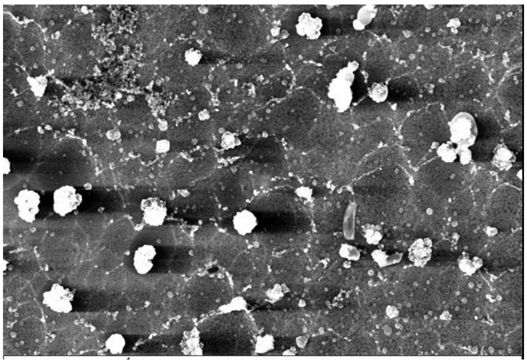


Figure 2. NPT on aluminium 6016,batch 1.

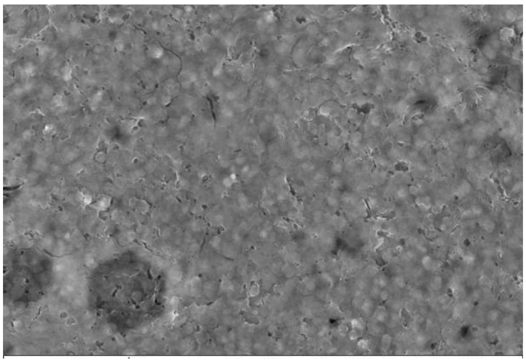


Figure 3. NPT on HDG,batch 2.

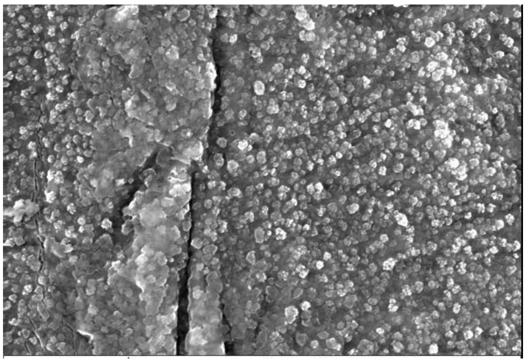


Figure 4. NPT on HDG,batch 2.

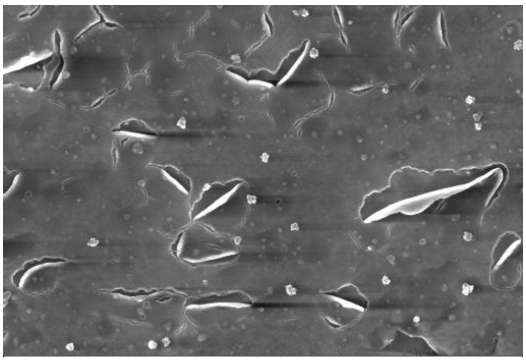


Figure 5. NPT on CRS, batch 3.

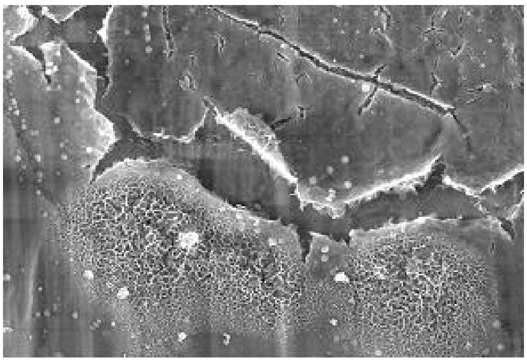


Figure 6. NPT on CRS, batch 3.

Defects of various kinds can be found on all substrates although the general impression is that more defects of serious kind were found on CRS than on aluminium. EDX analyses show that the delaminated areas do not have a coverage of pretreatment as the amount of zirconium is virtually zero.

ACT results 2010-2012

The results from accelerated corrosion tests were collected in figure 11-13. The results show that the new pretreatment systems pass the requirements on HDG and HRS but not on CRS.

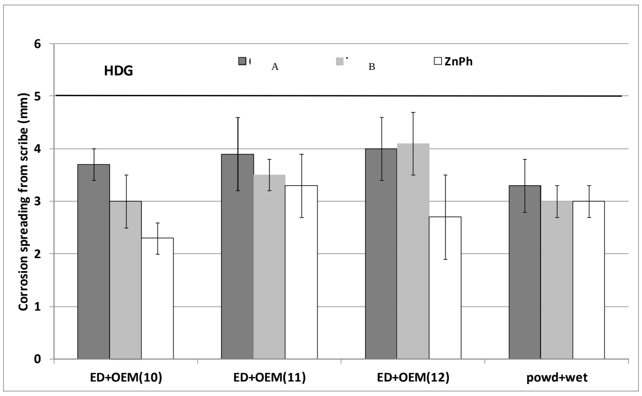


Fig 11. Summarized ACT results from HDG coated with the same paint system (electrocoat + 3 layer paint) for three consecutive evaluations as well as one paint system with powder primer and wet top coat. Requirement for passing is $\leq$ 5mm corrosion spreading.

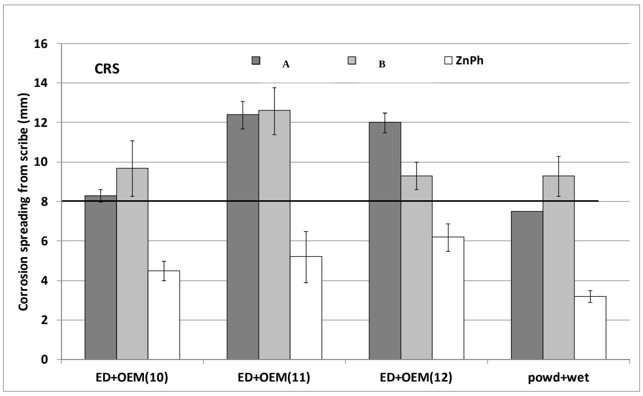


Fig 12. Summarized ACT results from CRS coated with the same paint system (electrocoat + 3 layer paint) for three consecutive evaluations as well as one paint system with powder primer and wet top coat. Requirement for passing is $\leq$ 8mm corrosion spreading.

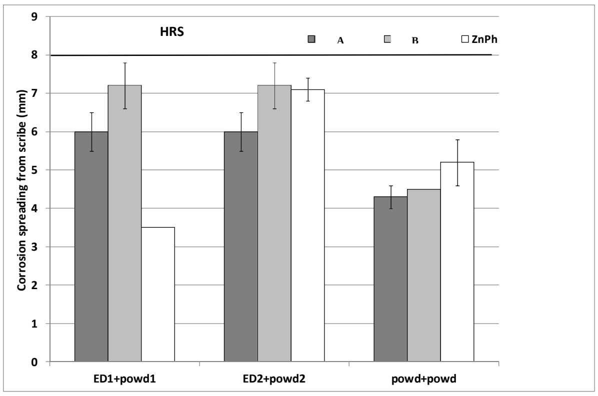


Fig 13. Summarized ACT results from HRS coated with three different paint systems. Two systems with different electrocoat and different powder to coat, as well as a system with powder primer and powder top coat. Requirement for passing is ≤ 8 mm corrosion spreading.

More extensive testing was performed on CRS due to the bad results shown above. Four different cold rolled steel substrates were tested, two of them with “improved” pretreatment systems provided by the suppliers. The results are shown in figures 14-17. Coating weights are also displayed in the diagrams (black columns).

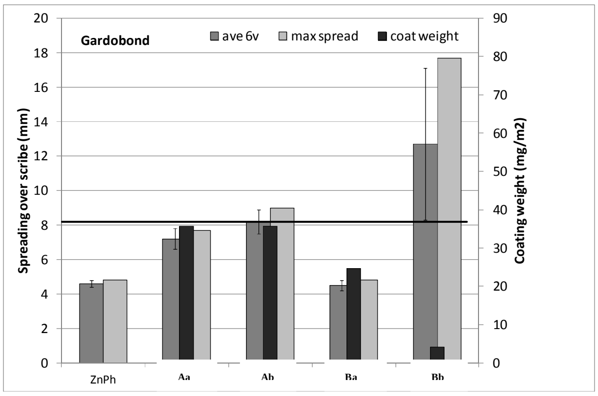


Figure 14 . Results from ACT test on Gardobond C (DC04), reference panels sold by Chemetall.

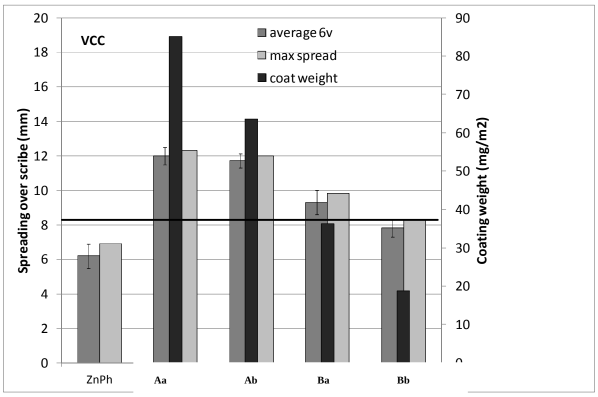


Figure 15. Results from ACT on VCCs cold rolled steel sheet material.

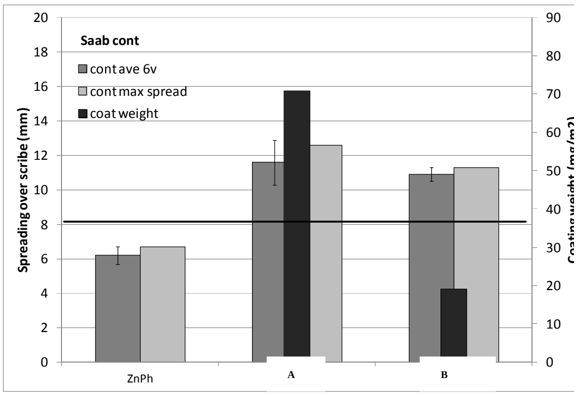


Figure 16. ACT results on Saabs' continuously heat treated sheet CRS

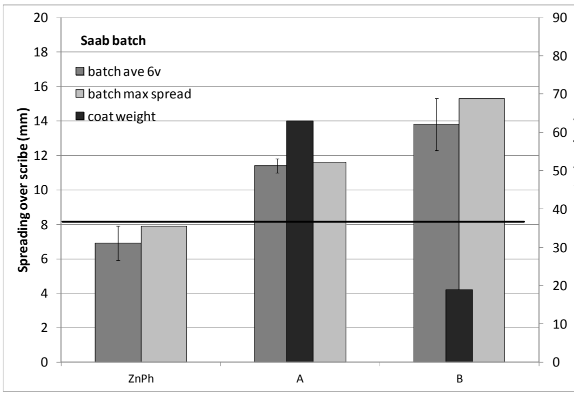


Figure 17. ACT results on Saabs' batch heat treated sheet CRS

The results on the substrate Gardobond C is surprisingly good for the new pretreatments. This is in agreement with many of the results that the suppliers present from tests in which this reference substrate is commonly used. The new pretreatment systems do not pass the requirements on any of the other cold rolled steel substrates.

Coating weights around 4-5 mg/m^2 is obviously too low which is seen on Gardobond treated with Bb. Coating weights around 20 mg/m^2 seem to be enough for B, while the coating weight seem to be higher for A. All of the coating weights except 4-5 mg/m^2 seem to be within range and does not have any major influence on the corrosion protection performance.

Panels for field test and Scab were prepared in "batch 1", the first evaluation that was performed 2010. The exposure period was October 2010 – May 2012 for field (June 2010- May 2012 for Scab) and the vehicle followed a route between Stockholm and Göteborg. The correlation between results from ACT1, Scab and field testing are shown in figure 18. There is a good correlation and it is reasonable to assume that ACT1 is a good accelerated cabinet test also for new pretreatments.

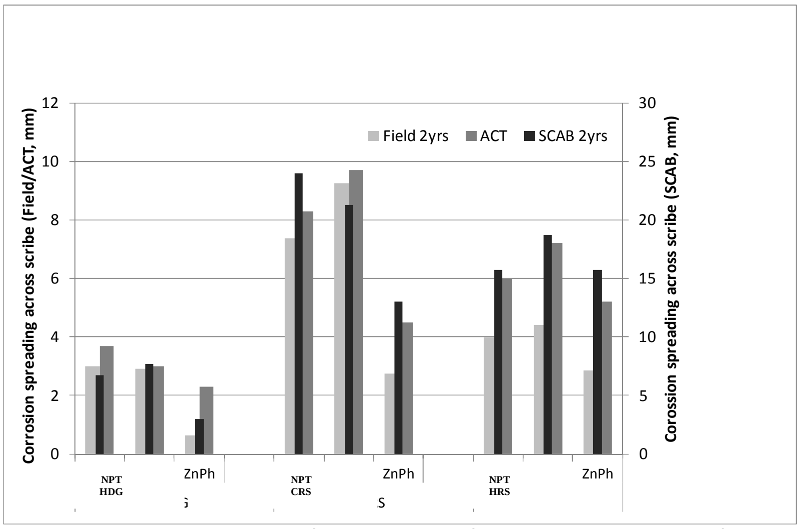


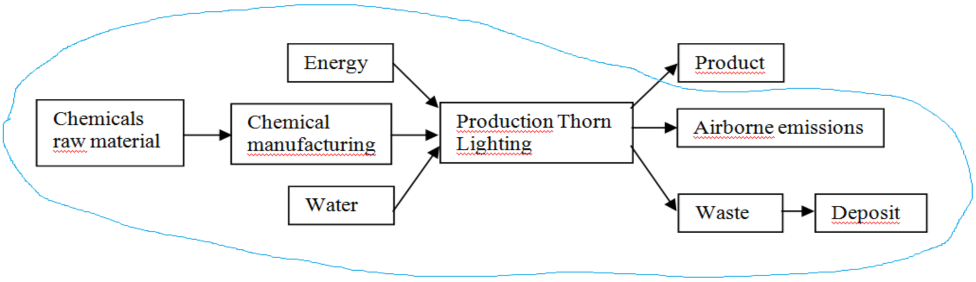
Figure 18. Correlation between ACT results from 2010 and field test with exposure from October 2010 till May 2012.

Corrosion products were identified by FTIR after ACT1 and field testing, respectively, and some conclusions could be drawn concerning the corrosion mechanisms. The findings can be summarized as follows:

- Similar corrosion mechanisms are found on panels treated with new pre treatment and panels treated with ZnPh.
- Anodic delamination is the dominating corrosion mechanism for all systems.
- Could differences in adhesion between pretreatment/paint and electrochemical properties explain the differences between the systems?
- Similar corrosion products are found after ACT1 and field tests

Energy and environmental aspects of new pretreatments.

A Life Cycle Analysis was performed on a small company that changed pretreatment from ZnPh to a new system. The system boundaries were put up as shown below:



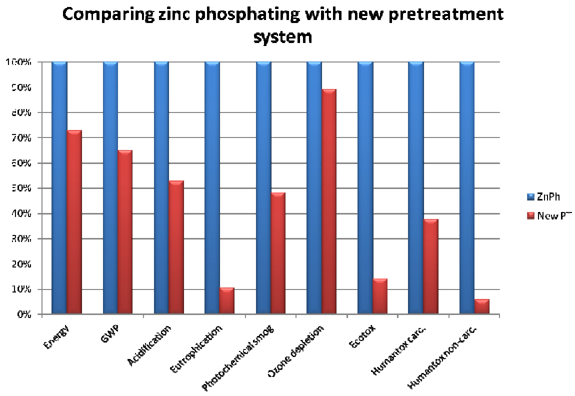


Figure 19. Comparison between ZnPh and new pretreatment. ZnPh was set to 100% for all parameters that were evaluated. GWP= global warming potential.

Figure 19 show all of the headings that are estimated in an LCA.
The financial analysis by the company gave the following conclusions:

- Less costs for chemicals
  - 49% reduction for chemicals only
- Less costs for maintenace
  - ~100% reduction for maintenance
- Less cost for heating of baths
  - 33% reduction for heating of baths
- Less cost for sludge
  - ~100% reduction for sludge
- Total reduction of cost
  - 47% reduction for chemicals, maintenace, heating and sludge

5.3 Discussion

A lot of effort in this project has been put into characterization of the new pretreatment systems. When the application was written for this project, there was a general understanding that the new pretreatment systems were ready for industrial introduction with small adjustments. The knowledge gained since then shows that the performance is not yet convincing.

One aspect of the project's management in connection to the results obtained is the fact that all panels have been prepared in Swerea IVF's pilot line with fresh baths set up by the suppliers each time (June 2010, February 2011, Nov 2011). During the project period, it has been pointed out by the suppliers that better results often are obtained when a line has been running for 3 months. This is due to the fact that some amount of for example Zn^{2+} or F^- ions have proved to be beneficial for the coating weight and corrosion protection. Low concentration of these ions will build up after some time when the line has been running. This fact can have an influence on the results when testing corrosion performance and should be kept in mind. It must also be emphasized that the numbers of evaluations and panels with each system have been limited. Since corrosion is a random phenomenon, testing a very large number of samples is the only method to compensate for the built in uncertainty.

Extensive characterizations have been necessary to gain knowledge about the new systems and also due to the need to find appropriate measures for qualification. Some characterizations such as coating weight measurements, adhesion measurements (Revetest) and FEG-SEM requires further experience in order to know the acceptable range (coating weight), the applicability (Revetest) or how the analysis should be performed in order to obtain most information and when to approve a system (FEG-SEM).

The FEG-SEM images reveal defects in the coating especially on CRS. These findings might have a connection to the bad results in accelerated corrosion tests of CRS. The suppliers will be contacted in order to get comments on the coating defects. Very generally, there seemed to be more defects in the “A” coatings than in the “B”coatings. The anodic polarization measurements generally ranked “A” higher than “B” but when comparing the ACT result the new systems perform about equally good/bad.

The LCA showed that substantial savings can be made by introducing a new pretreatment system. Savings concern mainly energy and reduced costs for waste handling but also costs for chemicals.

5.4 Delivery to FFI-goals

As shown by the results from the Life Cycle Analysis performed on NPT and described above, the project has verified the supplier’s information about the effect of introducing NPT in a surface treatment production. This is very important information for the vehicle manufacturers and the subcontractors since the economic benefit will make the change very attractive. The project results contribute specifically to the objective of the FFI program concerning the reduction of CO_2 emissions due to the reduction of energy consumption but also to lower acidification, eutrophication and general toxicity.

6. Dissemination and publications

6.1 Knowledge and results dissemination

Environmental legislation forbidding the use of Nickel in vehicle pretreatment would be a very important driver of change introduction of NPT. Another important driver can be the trend to use more light weight material such as aluminium or polymers in the vehicles. A third important factor is the desire to substitute zinc phosphate and electrocoating in the surface treatment of vehicles.

6.2 Publications

Presentation på ”Scandinavian Coating 2011”, April 2011, Copenhagen
Poster på ”Eurocorr 2011”, September 2011, Stockholm
Presentation ”Klusterkonferens” i Katrineholm, Maj 2011
Presentation ”SPF vårkonferens 2012”, Maj 2012, Västervik
Tidsskriften: Ytforum no 8, 2010
No 1, 2011
No 3, 2012
No 4, 2012
Industriel Overfladebehandling, Aug-Sep 201

7. Conclusions and future research

- ACT results show that the systems pass the requirements for hot dipped galvanized steel. However, the performance of materials pretreated with the new systems was in many cases inferior to phoshated materials. The results with the new pretreatment system were less repeatable and also more dependent on the paint system than phosphate material.
- From the tests performed within FFI New pretreatments and the “Enable project” it seems that a careful adjustment and testing must be performed in order to obtain good results for ED-coating new pretreatments. Powder primer seem to be a success factor as these systems generally gave good results in ACT
- The performance of the new pretreatments was poor for carbon steel and did not pass the requirements. On the other hand better results were obtained hot rolled steel which was sand blasted before pretreatment.
- Defects were found on pretreatment films on all substrates, but these were more serious on carbon steel when studied in FEG-SEM. This raise questions about overall performance, but especially for the long term behavior (~10 years).
- SCAB results on aluminium indicate that the performance of the new pretreatments is good but larger number of samples/accelerated test is needed.
- Supplier’s information on possible savings to be made has been confirmed as realistic by the switching from ZnPh to a new pretreatment system at a small company.
- Preliminary results show good correlation between ACT and field tests. FTIR studies reveal the same type of corrosion products and similar corrosion mechanisms are suggested.

Future research

- Addressing the question of *long term performance* is necessary. Panels for these tests should preferably be prepared in a line that is continuously running in order to get the bath parameters as optimized as possible.

- The larger variation in the results for the new pretreatments and sensitivity for the type of paint system should be studied in relation to the structure and composition to the pretreatment layer.
- Preparing panels in a running line would also answer the question of how much these results deviate from results obtained in a line with freshly prepared baths.
- Studies of the state of the surface for steel (detailed surface analysis), HRS and CRS in relation to various degreasing parameters should have a priority in order to better understand and optimize the performance on these substrates. It would be preferred to have a close cooperation with the suppliers.

8. Participating parties and contact person

Volvo Technology, Henrik Kloo (project manager)

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SAAB Automobile AB, Per-Arne Käck

Proton Technology, Göran Holmbom

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