“MASTERING THE ENVIRONMENT”

Developments in corr

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Whilst much of the earth’s crust is made up of metals in the form of complex oxides, pure metals are rare in the natural world. It is only gold and a few other stable metals that occur naturally in their elemental form. The more reactive “industrial” metals are used in an unstable state, and chemical reactions, predominantly with water and oxygen in our natural environment, will ultimately return them to more stable oxidised forms. This is natural “corrosion” and, for iron and steel, the result is RUST.

rosion (prevention)

Our weather, *"The Environment"*, is the driving force of natural corrosion, but conditions of exposure vary according to location. The natural stresses of temperature, humidity and rainfall, combined with the varied chemical cocktails in the atmosphere in marine, rural, urban, or industrial locations, result in a potent corrosive power against which our protective systems should be effective.

According to statistics from the International Corrosion Society (NACE), metallic corrosion costs the economies of the western world many hundreds of billions of dollars every year. The NACE study concludes that optimised use of technological improvements could save between 25 and 30% of this enormous corrosion cost. It is therefore a worthwhile objective to develop the most effective possible systems for minimising corrosion processes.

In addition to developments in the coating system, more fundamental choices for improving corrosion performance could include substitution with stainless steel, aluminium, copper or plastics, or coating with inert or sacrificial metals like zinc, aluminium or even lead. However, corrosion is not the only criterion for material selection, and due consideration has to be given to strength, stiffness, weight and, not least, cost. Accordingly, paint and organic coatings retain an important role in corrosion protection, especially for steel-based substrates.

Environment-friendly performance

For more than a hundred years the traditional treatment for iron and steel was to apply a generous coating of a paint based on linseed oil and red lead – and to repeat the operation every couple of years. This was labour intensive and an inefficient use of materials, quite apart from any considerations of toxic hazards.

For almost 50 years, most high performance coating systems have been based on chromate chemistry, both in chemical pretreatments and in paint pigmentation, but in the last decade there has been an increasing environmental pressure away from chromates because of their toxic effects and the resulting alarming labelling requirements.

Once again *"The Environment"* is a driving force, this time for product development with maximum performance and minimal environmental impact.

"The Environment" pushes towards better and more effective products, and pulls towards non-hazardous, non-polluting formulations.

We must strive to Master The Environment in its corrosive effects…

…. but The Environment is the Master of what we can use.

This situation is common to all business sectors, but none more so than coil coating, where long product life, cleanliness, safety and the environment are all positive marketing features.

We have to develop new, effective, environmentally benign coatings and we don't have too much time…

The anticipated restrictions governing the use of chromate pig-

Panorama view of the Bohus Malmön natural weathering site on the west coast of Sweden.

ments have made our customers keen to find alternatives: "We need a new primer! It needs to be more effective than the current version, free from any toxic or hazardous components. It must be more economical to use. It must be able to sustain a 20 year warranty. Universal, of course – and we can't wait long for the answer. Oh…and we'll need a new pretreatment system too".

And the established coil coatings demands must also be maintained: high adhesive strength and high-flexibility – but no chromate.

Several factors limit the choice of alternative anti-corrosive materials:

- Effective in thin coatings
- Stability with established cure chemistries
- Effective on galvanised steel.

Many of the available chromate-replacements are based on zinc phosphate, sometimes modified with orthophosphate hydrates and with other metals such as aluminium, calcium, magnesium and molybdenum. There are also polyphosphates, molybdates, metaborates, organo metallics and even ion-exchange pigments. Organic anticorrosive synergists are also offered.

Becker has focused on this primer development work since the late 1980s and early nineties. Several trials were conducted at coil coating lines around Europe using chromate free primers. In all cases, panels were exposed both in accelerated test cabinets as well as natural external environments.

When looking for alternative chromate-free pigments for our primers, it was kept in mind that these are only one part of the overall coating system. Most chemical pretreatment today is chromate based, and this is also being reformulated.

For many years, Becker has been liaising closely with the major pretreatment suppliers to develop a compatible chromate-free package, and such a system has been in limited commercial use for some years.

There is strong demand for fast-answer accelerated corrosion tests, and we are all sceptical about their value. Generally, the faster the test and the higher the acceleration factor, the lower the chances for good correlation to natural conditions.

During the Technical Committee meeting at the 2001 Congress in Brussels, Mr Hoeflaak and Mr. Tiemens, of the TNO, summarised a major ECCA-sponsored study of five and ten year natural- and laboratory-based weathering. Testing included salt spray, Prohesion (with and with-

Conditions of exposure vary according to location: marine, rural, urban, or industrial. Becker coating systems must protect substrates from a potent chemical cocktail of atmospheric pollutants and solar radiation.

out QUV) and specific industry and TNO protocols.

Evaluations were made on the face of the panel, the edges, scribes and fastenings, in a very detailed and exhaustive study.

A more fundamental and scientific approach to corrosion testing may be made with electrochemistry,

No usable correlations were discovered for any systems on galvanised steel – and even on aluminium the results were not conclusive.

measuring conductivity, capacitance and impedance during a period of exposure to corrosive stress .

Specific local corrosion resistance at edges, scribes and other deliberately induced defects can be evaluated with scanning electrochemical techniques.

But can this provide the confidence to predict real product lifetimes?

Natural weathering is not a controlled process, we can record the rainfall, the temperature, hours of sunlight, panel temperatures, and we can attempt to incorporate this data into our laboratory testing, but we cannot incorporate the element of disorder, of natural chaos.

For the foreseeable future we will definitely need the support of real-time natural exposures at aggressive locations over extended periods of time. Becker has gathered tremendous experience through the exposure of thousands of panels over very many years, at Bohus Malmön on the west coast of Sweden.

Accelerated v. natural weathering

In 1997 we began an ambitious project to compare current and developmental pretreatments and primers applied to the three main ferrous substrates and finished with the three most popular topcoats.

HDG (Hot Dip zinc-Galvanised steel), Galvalume (45/55 zinc/aluminium coated steel) and Galfan (95/5 zinc/aluminium coated steel) were sourced from different steel producers, our pretreatment partners in the project then applied fifteen different (9 chromate-free) products. No less than 59 primers were evaluated, commercial and in development, of which 30 were chromate free.

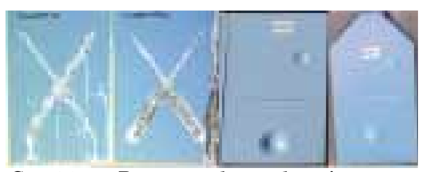
Full coverage of all possible permutations would have totalled 7965 systems! A statistical experimental design was used to make the exercise more manageable, but even so, nearly eight hundred combinations of substrate, pretreatment, primer and topcoat were prepared.

Accelerated testing was based on ASTM B117 salt spray (continuous fog at 35°C) and ASTM G85-A5 Prohesion (one-hour cyclic fog – unheated – and one hour dry at 35°C). Bohus Malmön exposures were made in two orientations: traditional 45° South facing and vertical North "under eaves".

Little correlation of test results

Now, after four years exposure, our findings have confirmed those of the TNO study: there is little correlation between laboratory-based testing and natural conditions.

Some systems that were poor in accelerated tests are still performing well at Bohus Malmön after four years exposure…



Cw4397 – Poor accelerated testing – good natural.

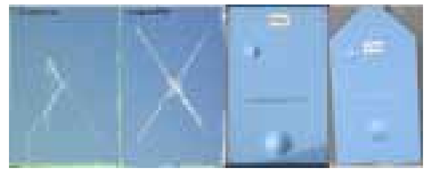
…and others, which perform well in salt spray, actually perform worse in the field.

Cw4901 – good accelerated tests– bad at Bohus Malmoen

In these pictures the test panels are, from left to right: Neutral Salt Spray, Prohesion, North-facing and South-facing Bohus Malmön (four-years) exposure.

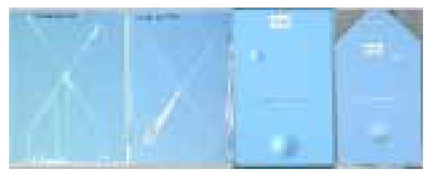
The same scheme is used in the following sets, illustrating the progression from a current "standard" chromated system, through partially chromated "Hybrids", to a totally chrome-free development.

All of these illustrations are on HDG substrate.

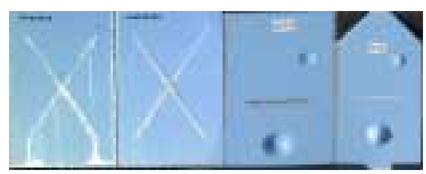


Cw 4102 - Conventional System- chromate pretreatment / chromate primer

Generally most of the fully chromated systems perform quite well.

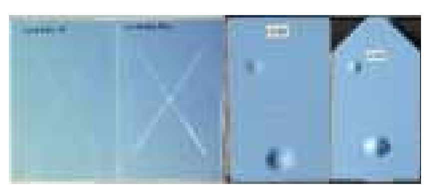


Cw 4100 - Hybrid I chrome-free pretreatment – chromated primer



Cw 4519 - Hybrid II chromate in the pretreatment – chrome-free primer

Several of the hybrid systems are still performing well: the chromate is effective in whichever layer it is present.



Cw 4586 - No chromates anywhere!

A small number of totally chrome-free systems show very good performance.

University Studies

Our investigations have not been confined to performance testing. We are working to gain a better understanding of the fundamental mechanisms of adhesion and the physical and chemical interactions between paint, pretreatment and metal surface. We are also examining the roles of the different formulation components. In this work we have used surface analytical expertise provided by the University of Surrey based on X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) analysis.

Using a combination of these two techniques we are better able to understand the adhesion mechanisms at the pretreatment/primer and primer/topcoat interfaces, and so formulate more successful systems.

Summary

From this extensive programme we can identify some successful examples of chromate-free systems in the field and can immediately offer suggestions to customers wishing to move away from conventional chromate-containing systems. For lines retaining a chrome containing pretreatment this generally produces few difficulties.

If a chrome-free pretreatment is also to be used, it is necessary to refer to the ongoing exposure series to check compatibility and interactions.

- Chromate-free pretreatments and primers can be produced successfully and with a high level of anti-corrosive activity. The difficulty is in getting the two to work together, as these systems are in general more critical for substrate, paint and pretreatment combinations than chromated systems. Chromates are more forgiving, but chromate-free primers can be produced which are as effective as their chromate containing analogues, providing sufficient attention is paid to these interactions and in material selections.
- Polyurethane primers, both conventional and high-build, are generally most successful when it comes to incorporating the new chromate-free pigments. Based on the tests that we have carried out, we have seen some systems performing at a similar level to chromates.
- Chromate-free epoxy primers can be produced but their inherently lower flexibility introduces points of weakness for corrosion initiation at micro cracks in severely formed areas.
- Due to the limited choice of resins that can be used in primers for PVC plastisol, totally chrome-free combinations are more difficult to produce. Further work is ongoing in this area, to produce a completely successful system.
- The search for improved performance is our constant goal. Several hundred more panels have been put on exposure at Bohus Malmön since 1997. These are evaluated on a regular basis, ensuring that products we offer always have optimum performance.
- Now more than ever before, there is a real need for improved communication and collaboration between suppliers of paint and pretreatments and the metal producers and coil coaters
- Accelerated tests generally favour chromates, but the true answer to anti-corrosive performance in service can only be gained from real natural exposures. After 4 years in an aggressive marine exposure we have many systems which are performing very well.
- The panels that face north "under the eaves" are generally the worst in natural corrosion.
- It is unlikely that a single pigment will replace strontium chromate. It has been found necessary to use a combination of two or three pigments together to give a synergistic effect.
- Higher pigment loadings do not automatically lead to improved corrosion resistance, levels must be optimised. This is also very important from a commercial viewpoint, due to the relatively higher cost of the new materials, the inclusion of excessive amounts could make the primer economically unattractive.
- The results shown here focus on one substrate, HDG – in general our studies suggest that better performance is obtained on Galfan, but that Galvalume is a difficult substrate for chromate-free systems.
- It cannot be assumed that a particular combination that works in one resin system over a particular pretreatment will also work in different resin/pretreatment combinations. This leads to a self-perpetuating search for "The Best Chromate-Free Primer" as "new improved" raw materials are offered by suppliers. Hundreds of new permutations are currently being evaluated in this most recent phase of our exposures.

Competing with a relentless adversary

So: are we beginning to "Master the Environment"? There are some indications that we are at least making progress towards our goal, but we should never become too confident.

Something of the uncertainty of the situation is shown in the fact that Zinc compounds are now seen as hazardous, as the zinc ion has toxic effects to aquatic organisms (EU Directive 67/548/EC – June 2002). We have to re-examine our progress and the implications of this legislation. We should realise that our adversary has billions of years of experience, but with careful study and determined effort we have improved our understanding and can compete on more equal terms with our Master, the Environment.

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