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FILIFORM CORROSION : MECHANISMS AND SOME POSSIBLE CONSEQUENCES

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ABSTRACT

The mechanisms of degradation at defects of organic coatings (scratches, impact damages, cut edges, drilled holes etc.) are discussed on the basis of the results of several investigations on filiform corrosion, of edge creep corrosion and corrosion at cut edges. Similarities with crevice corrosion are underlined. It is observed that the most advanced front of the degradation is not visible with the naked eye. The consequences on test methods, protection or mitigation methods (primers, properties of the paint film) are presented. An explanation is given for some unique characters of filiform corrosion. Practical applications in the paint industry may result in better performances.

Key-words : filiform corrosion, crevice corrosion, edge-creep, cut edges, organic coatings

INTRODUCTION

It is a common observation that some coatings develop large and early degradation at scratches, at impact damages or at cut edges, drilled holes, bent profiles etc. On the contrary, other types of coatings resist much better under the same circumstances. There is a frustration in not knowing more on the reasons for these differences in behaviour.

The combination of the results of several fundamental or applied researches provides some useful insight on the mechanisms of corrosion at organic coating defects. These studies dealt with the mechanisms of crevice corrosion, the filiform corrosion of aluminium and steel products, the edge-creep corrosion of painted Al-Zn coated steel, the corrosion at cut edges of coil coated products [1,2] and with investigations of the corrosion of brake tubes coated with polymers.

Due to limited funding, the different aspects of the degradation processes at coating defects were studied on different systems : the influence of the mechanical and physical properties of the coating was extensively studied for the filiform corrosion of aluminium, specific test methods were developed for filiform corrosion and for edge creep corrosion and electrochemical parameters were considered in all cases.

A typical example of filiform corrosion of aluminium is shown in figure 1.

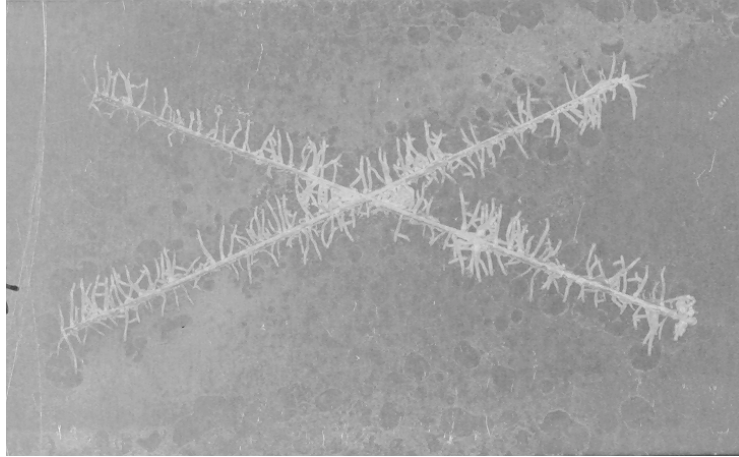


Figure 1 : Typical aspect of filiform corrosion on aluminium
(the organic coating was removed by pyrolysis)

EXPERIMENTAL

The mechanisms of crevice corrosion were studied with an experimental assembly that allows to measure the pH and the potential and to analyse the solution inside a crevice, and to measure local currents from and to the crevice, as a function of the potential imposed to the whole. An example of the experimental set-up is shown in [figure 2](#) [3].

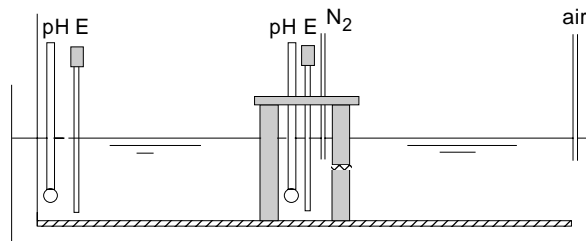


Figure 2 : Artificial crevice, with E and pH measurement in and out of the crevice

The metal is pure iron. The solution is originally $\text{NaOH } 10^{-3} \text{ M} + \text{NaCl } 10^{-3} \text{ M}$. Crevice corrosion is started by purging with nitrogen the solution in the artificial crevice, while the rest of the surface is exposed to the aerated solution. As corrosion in the crevice develops, the potential, the pH, the solutions composition in and out of the crevice and the coupling current are measured.

Filiform corrosion was investigated on Al 5005 plates chromated with Cr^{6+} (Aludan, Belgium) and coated with several carboxyl polyester powder coatings containing 1,3,5-triglycidyl-isocyanurate (TGIC) as hardener, plus titanium oxide, benzoin and a solid phase spreading agent. The cure was at 200°C .

The filiform corrosion tests were conducted according to the GSB procedure (Gütegemeinschaft für die Stückbeschichtung von Bauteilen, Schwäbisch Gmünd,

Germany) : a cross scratch is made through the coating, the plates are first exposed horizontally above a 33% HCl solution with the scratch facing downwards for one hour at room temperature. The plates are then dried without rinsing, then transferred to a humidity cabinet (40°C, 80% RH) for 1000 hours. After the test, the potentials in the filaments under the coating were measured with a cactus thorn needle capillary linked to a reference electrode and the pH was measured after freezing the plates with dry ice, removing the coating and applying a coloured indicator on the filaments.

The influence of a series of parameters on filiform corrosion was studied : the surface conversion treatments, the pigments and hardening agents, the permeability of the coating to oxygen and water, possible physical and chemical aging effects such as a prolonged contact with water, with acid solutions as formed in the head of the filaments, or with strongly oxidizing agents as the chromate conversion treatment. A full report of these influences is given elsewhere [4,5].

The edge creep study was conducted on aluzinc (55% Al, 43.5% Zn, 1.5% Si) coated steel, with a strontium chromate pretreatment before coating. The coated panels were cross-scratched down to the aluzinc coating but not to the base steel. The scratched area was exposed to aerated 0.6 M NaCl, coupled to platinum. Platinum is used to simulate and exacerbate the coupling with the cut edges of the aluzinc coated steel. These cut edges act as a more noble metal compared to the scratched aluzinc, in most atmospheres. The test lasted for 45 hours ; the electrical charge passed between the Pt and the scratched AlZn, and the aspect of the scratched AlZn were the outputs of the test. The edge creep test arrangement is illustrated in [figure 3](#).

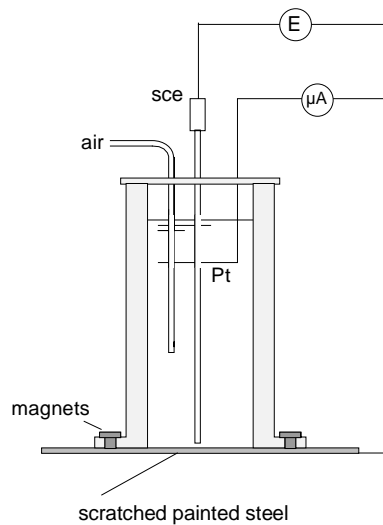


Figure 3 : Experimental assembly for edge creep corrosion testing

RESULTS

Crevice corrosion of iron

[Figure 4](#) shows the changes of pH and potential inside the crevice as crevice corrosion develops. Initially the solution is alkaline and very diluted in chloride (10^{-3} M). When crevice corrosion is stabilised, the pH is around 3.5 and the chloride concentration

approaches saturation (9 M or 319 g/l at 25°C). The active crevice, at low potential, is coupled to the surrounding aerated surface which has a higher potential and therefore the corrosion rate can be very high in the crevice [6].

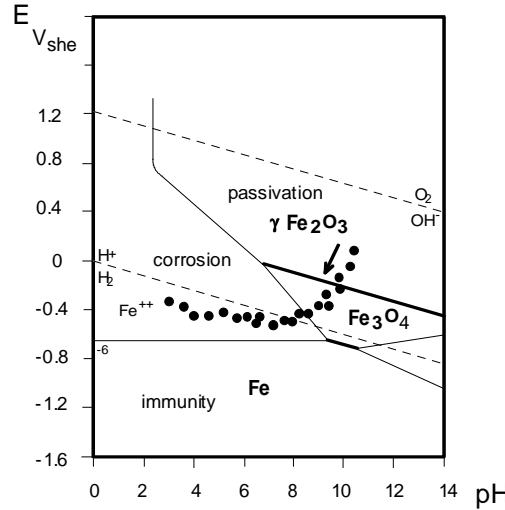


Figure 4 : Changes in pH and potential in an active crevice of iron

Filiform corrosion of aluminium

At some stage, some filaments were pierced in the head or in the tail, with a needle. In other cases, a scratch was made ahead of the head, and the progression of corrosion was observed.

In spite of the difficulty of the measurements, it was confirmed that filament heads are acidic and have a low potential, and that the tails are neutral or more alkaline, with higher potentials (figure 5).

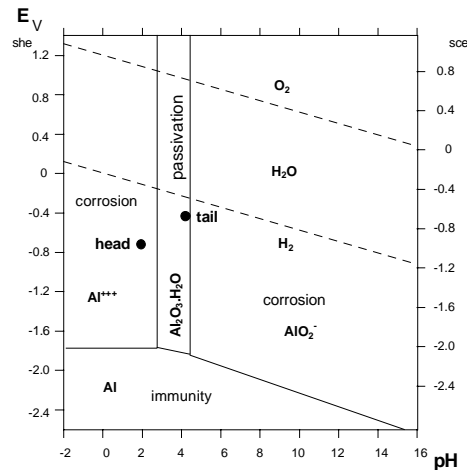
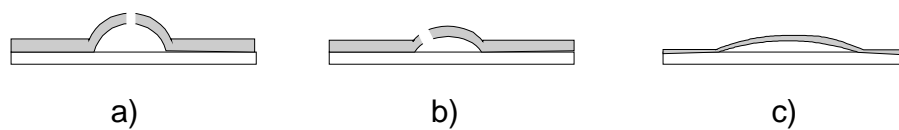


Figure 5 : Potential and pH in heads and tails of filiform corrosion of aluminium

The observation of a large number of filaments indicated that:

- some coatings exhibit filaments that have cracks in the heads. These filaments generally remain short. The cross section of these filaments looks like in [figure 6a](#), with some kind of semi-circular profile.
- some other coatings exhibit non-cracked. These filaments continue to grow and generally give bad results in the filiform corrosion test. The cross section of these filament looks more like in [figure 6c](#), with a tapered cross section.
- piercing the head of the filaments of some paints did not necessarily stop their progression,
- in some cases, scratching the paint 0.5 to 2.0 mm ahead of the visible head resulted in an immediate stop of the progression,
- filaments grow without crossing or merging with each other ([figure 1](#)).



[Figure 6](#) : Different cross sections of filaments in filiform corrosion.

a) good adhesion, ductile. b) good adhesion, brittle. c) poor adhesion, good mechanical resistance. Filaments 6a and 6b generally do not grow much. Filaments 6c grow longer.

Edge-creep of Aluzinc

pH measurements under the damaged coating were made by freezing the plates on dry ice and carefully removing the paint debris and then applying a gel made with a colour pH indicator. Acid pH (about 3.5 to 4.0) were found at the front of the coating degradation and a higher pH at the back, near the plate edges. Potential at the front of edge creep was difficult to measure (probably because of very large local currents and an important ohmic drop error) but it was estimated from the observation of significant hydrogen evolution.

When the accelerated edge creep test was just finished, the samples showed only some detachment of the coating very near the scratch. But on the next day, after the samples were allowed to dry in the laboratory, beautiful four-leaved clovers could be seen, drawn by a regularly dotted line created by small crystals formed underneath the paint. This aspect is represented in [figure 7](#). The same test conducted in bicarbonate solution without chloride showed no damage.



[Figure 7](#) : Aspect of cross-scratched sample after edge creep testing (four-leaved clover)

DISCUSSION

Filiform corrosion, edge creep corrosion, corrosion and cut edges and many types of corrosion at defects of organic coatings are special cases of crevice corrosion. Oxygen has a rather easy access to the exposed surface of open defects (the mid-line of a scratch, the edges of a cut plate or the sides of a hole etc.) and its access to thinner recesses underneath a disbonding coating is much more difficult.

Cathodic reactions (oxygen reduction) prevail at the exposed surface, while anodic reactions (corrosion of the substrate) prevail at the tip of the recess, at the advancing front of the disbondment.

Similarly to the crevice corrosion process, the anodic zones become acidic, with an increase of the chloride and metal ion concentrations and some hydrogen may also evolve there. Metal dissolution and hydrogen production produce the major part of the damages to the coating. The cathodes are located behind the local anodes, where there oxygen is reduced with an alkalisiation. This alkalisiation may add to the damages.

The important observation is that the local anodes are far ahead of the visible damages. This was clearly shown during edge creep testing ([figure 7](#)) : the visible damages were just the scratch, which is more or less wide depending on the test duration. But the real front of the advancing corrosion process is the dotted line looking like a « four-leaved clover ». This dotted line was formed by the precipitation of AlCl_3 crystals, when the concentrated solution of Al^{+++} and Cl^- was allowed to dry. In fact, corrosion and hydrogen evolution have detached the coating from the substrate on the whole surface between the four-leaved clover and the cross-scratches. The activity of the corroding zone at the front is enhanced by the coupling to more aerated surfaces, close to the scratch.

The same is also true for filiform corrosion of aluminium.

Piercing the head of a filament does not always stop filiform corrosion : the true anode is far beyond the head. The visible head is more aerated than the true anode and piercing the head does not change much in the operation of the occluded cell. The schematic representation of filiform corrosion should be revised to show the importance of the very narrow detachment of the coating ahead of the visible damages ([figure 8](#)).

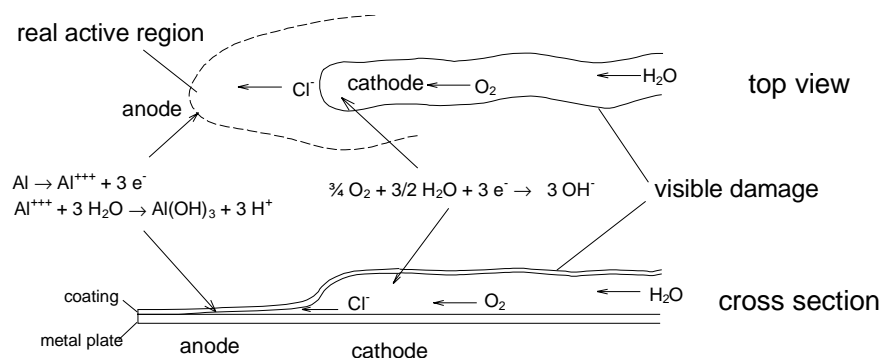


Figure 8 : A revised representation of the reactions and geometries in filiform corrosion of aluminium

A scratch ahead of the visible head can stop filiform corrosion : when the invisible true anode reaches the scratch, it suddenly becomes aerated and the acidification process is stopped.

Filaments generally do not intersect : in [figure 9](#), the visible filaments are drawn as continuous lines and the real active anodic zones are represented as a dotted line, ahead of the head. This is the only acid and actively corroding region. Some hydrogen is evolved there. All the other regions are more alkaline because of oxygen reduction. The right part of [figure 9](#) shows a filament Y approaching the filament X : when the active anode in front of the head of Y meets the sides of the tail of filament X, some oxygen from the tail of X reaches the anode of Y. This neutralises the acid at the contact point. Thus, the acid front of filament Y moves towards the less aerated region and this causes the filament Y to make a sharp turn away from filament X. This is indeed observed in practice. In fact, the visible parts of the filaments seem to avoid each other, but the invisible parts come in real contact at one point. The mechanisms of occluded corrosion cells command the active anode to strictly avoid oxygen.

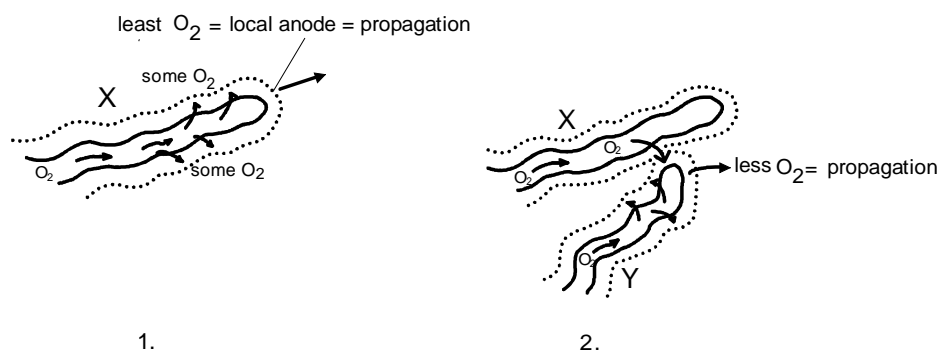


Figure 9 : Schematic presentation of the propagation of filiform corrosion.

1. Filament X with visible contour (——) and the active anodic zone (-----)
2. Filament Y approaches filament X and changes direction (opposite of oxygen ingress)

The occurrence of filiform corrosion (on steel or on aluminium) depends on a number of factors including the presence of some chloride, an average humidity or alternate wet and dry periods and some ill defined properties of the organic coating.

The work done during the study of filiform corrosion of aluminium indicated some of the properties of the coating that are important for filiform corrosion: when corrosion and hydrogen tend to detach the coating film, the filaments will show different shapes : well adhering and more ductile coatings will deform to show a cross section as in [figure 6a](#). In the end, the elongation of the coating is such that it cracks and this stops the propagation of filiform corrosion. Well adhering and brittle coatings show a similar behaviour: even under a small strain, cracks form and the process stops ([figure 6b](#)). On the contrary, poorly adhering coatings with a high tensile stress will not deform much and will not crack ([figure 6c](#)). This leads to a poor resistance to filiform corrosion. This means that the thickness of the coating is another important parameter for filiform corrosion : thicker (and thus more resistant) coatings may not be favourable against filiform corrosion.

Figure 10 shows an E-pH diagram for chromium with the indication of the conditions at the local anodes of damaged coatings. It is seen that, in these conditions, chromate Cr_2O_3 is soluble. Another fact is that filiform corrosion often progresses underneath the chromate layer, suggesting that Cr_2O_3 acts as a cathode. It may be that other primers are more suitable against filiform corrosion. Molybdate was proposed for this application and other systems may do the job also.

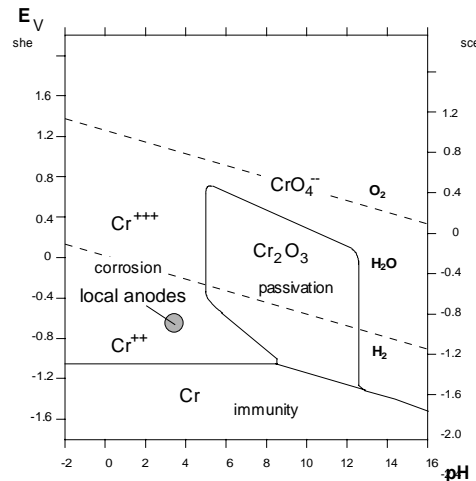


Figure 10 : Potential-pH diagram for Cr compounds with indication of the conditions in the local anodes of edge creep of AlZn and filiform corrosion of aluminium.

CONCLUSION

The results of studies of different corrosion processes (crevice corrosion, edge creep corrosion, cut edge corrosion and filiform corrosion of steel and aluminium) brought some new understanding of the degradation processes at coating damages.

An analysis of these corrosion processes suggests that electrochemical corrosion takes place at very thin recesses under the coating, far beyond the visible damages.

This analysis suggests some corrosion mitigation methods.

Some methods relate to the conversion treatment : chromate dissolves in low pH and low potential conditions and thus chromate is perhaps not most appropriate. Other inhibitive primers can be found among products that are efficient in occluded corrosion cell phenomena. There is an opportunity to change chromate for something altogether more efficient and more friendly to the environment.

Another approach is a correct combination of adhesion, mechanical properties and thickness of the coating.

The role of hydrogen production must be reexamined : hydrogen is not the cause of high pH and possibly of saponification of some coatings. In the occluded corrosion mechanism, hydrogen evolves essentially at the acid anodes. If the anodes are suppressed or deactivated, the hydrogen problem will be controlled.

The development of methods to mitigate a broad range of damages to coatings (filiform corrosion, corrosion from scratches, stone impact...) would certainly benefit from the contribution of electrochemistry.

Improved testing methods and qualification methods can be developed from the above considerations for specific types of corrosion damages.

Practical applications may be of interest to the coating industry.

The scientific contribution of N.Heymans and J.L.Delplancke (Université Libre de Bruxelles) and of D.Maetens (UCB Chemicals) to the study of filiform corrosion is gratefully acknowledged.

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