SELF-HEALING COATING SYSTEMS FOR CORROSION PROTECTION

Anthony Hughes†, Scott Furman†, Tim Harvey†, Simon Hardin†, Penny Corrigan†, Fiona Scholes†, Tim Muster†, Paul White†, Hartmut Fischer*

† CSIRO Manufacturing and Materials Technology, Corrosion Science and Surface Design, Private Bag 33, Clayton South MDC, Victoria 3169, Australia

* TNO Industry and Technology, Materials Performance, De Rondom 1, 5600 AN Eindhoven, The Netherlands

e-mail: Tony.Hughes@csiro.au, hartmut.fischer@tno.nl

The requirements for a self healing primer paint system are discussed in terms of the general aspects of inhibitor formulation and delivery to a defect in a paint system. For repeated healing of the underlying metal it is necessary to have triggered release of the inhibitor. This can be obtained through the delivery system which might be designed to respond to external triggers such as mechanical damage, moisture or chloride concentration.

Keywords: self healing, chromate replacement, paint, delivery systems

1 Introduction

Corrosion protection by paint systems is currently achieved by passive (barrier coating) and active (inhibitor) protection [1-4]. A breach in the coating allows ingress of water and corroders into the paint system, dissolution of the inhibitor, and release into the defect which repairs, or heals, the corrosion [4, 5, see also paper by Scholes et al. from these proceedings].

A common inhibitor incorporated into the primer is chromate, which is extremely effective for corrosion protection [6]. However, environmental and health concerns are driving the search for replacements to chromate in coating formulations [1, 7-14]. Alternative inhibitor systems are therefore a very important aspect of the design of self healing coatings.

2 Design of self healing coatings

Ideally, for self-healing of defects in coating systems, it is desirable to have a component to inhibit corrosion of the underlying metal and also to repair the polymer coating. The current design of paint systems, however, only offers repair for the underlying metal. For protection of metals, many paint systems consist of an inhibited primer and a topcoat. The repair function is usually achieved via release from the inhibited primer. The release of inhibitor from the primer leaves an inhibitor depletion zone within the primer [5] as depicted in Fig. 1.
Thus a large dose of inhibitor is released initially but low levels of inhibitor may persist over long periods of time even up to a few years [15, see also paper by Furman et al. presented in this proceedings]. Nevertheless, the large initial dose of chromate inhibitor is, essentially, a one-off process.

![Diagram of inhibitor-containing coating system](image)

**Figure 1:** An inhibitor-containing coating system – depletion of the active component (inhibitor)

Given these factors, some of the design features required for a self healing coating include:

1. The triggered release of the inhibitor to achieve multiple dosing at the corrosion site. The ability to obtain triggered release will involve design of the inhibitor system as well as its delivery system, the latter of which may provide the trigger mechanism.

2. Replenishment of the inhibitor depletion zone. This function will be inextricably keyed into the self repair mechanism of the polymer coating.

3. Self repair of the protective coating, which allows replenishment of the inhibitor at the former defect site.

The following sections are devoted to discussing these issues in more detail.

### 3 Inhibitors

As discussed previously, the release of chromate inhibitor from a primer results in a large initial dose, but lower levels of release as time increases (Fig. 2). Sinko proposed that the activity of inhibitor pigments can be qualified by the *inhibitor activity parameter:*

\[
I_i = n \frac{c_{sat}}{c_{crit}}
\]

where *n* is a stoichiometric factor, *c_{sat}* is the saturation concentration of the inhibitor and *c_{crit}* is the critical concentration of the inhibitor. As can be seen in Fig. 2, eventually the release of inhibitor falls below the critical concentration to prevent inhibition and the inhibitor becomes unable to prevent further corrosion.
The critical concentration can be ascertained a number of ways. In Fig. 3, a multi-electrode system (see paper by Muster et al. presented in this proceedings) has been used to determine the corrosion current on a number of metal electrodes. Fig. 3 shows the response for aluminium alloy 2024-T3 as well as mild steel. It can be seen that the corrosion current decreases with increasing cerium chloride concentration up to around $10^{-3}$ M which can be taken as close to the critical concentration for corrosion inhibition.

Cerium chloride, however, is extremely soluble and not suitable for direct inclusion into a primer paint system. Other compounds are also under trial including cerium (III) dibutylphosphate and cerium (III) iodate [12-14]. These compounds are much less soluble. For example, cerium (III) iodate, with a low solubility of 1.6 g/L, is more suitable for incorporation into a paint system. The release rate for cerium iodate in an epoxy film is depicted in Fig. 4 at two different pH values. At both pHs, the amount of inhibitor released goes through a maximum, however, in the acidic environment much more material is released.
This is desirable since one trigger for release is the low pH created at corroding sites. In addition, cerium dibutylphosphate and cerium iodate are multifunctional inhibitors. They display both cathodic inhibition, through the cerium ion, as well as anionic inhibition, through the anion (dibutylphosphate or iodate).

Figure 4: Release rate of cerium (III) iodate from an epoxy film. The amount released is similar to that from a SrCrO$_4$ inhibited primer [4]. The test area was 18.8 cm$^2$.

On the other hand, the release rate of a very soluble compound might be controlled via a delivery system. Encapsulation has been proposed as one type of delivery system [16]. However, this type of system tends to offer one-off repair and also displays problems with mixing during formulation. Other types of delivery systems include high surface area material, such as nanoparticles, ion exchange materials such as clays, zeolites and hydrotalcites [12, 16] or mesoporous materials. For these categories, there are several avenues for the delivery mechanism:

1. For sparingly soluble materials, ultramilling can produce a nanoparticulate powders that have a different rate of dissolution from the bulk.
2. Alternatively, the inhibitor can be adsorbed onto the surface of nanoparticles, exchanged into ion exchange materials or absorbed into the pores of porous materials.

For the materials with larger pores, it may be necessary to “gate” the pores with chemicals that respond to triggers such as a change in pH, moisture, or Na$^+$ or Cl$^-$ ions. It may also be possible to formulate an adsorbent which degrades in contact with moisture or other triggers to release the inhibitor. An example of a mesoporous ceria material is shown in Fig. 5.
4 Paint repair

The final step of the repair mechanism is achieved if a protective surface coating (after release of the corrosion inhibitor needed for primary inhibition) can be formed or rebuilt. In this case, the coating is not necessarily the same as the original coating. However, passive protection, prevention of further leakage of inhibitor, and a refreshment of the inhibitor level adjacent to the originally damaged area all must be realized (see Fig. 6).

5 Conclusion

This paper has outlined criteria to be applied to the development of self healing coatings. The requirements of new generation inhibitors and methods for their incorporation into a paint system, either directly or via delivery systems, have been discussed.
REFERENCES