

Dual-purpose defenders

Organic polymers protect metals in both thin layers and coatings

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Novel polymeric inhibitors have been shown to provide corrosion protection for several types of metal. They were effective both when applied as microscopically thin polymer layers and as synergistic additives to anti-corrosive coatings.

The functionalities of a coating system [1] depend on the make-up, internal structure, and hence ultimately the chemical composition, of that coating system. These properties change during curing and also properties close to interfaces (the substrate and the exposed surface) may differ from the properties inside the coating layer. The coating layers must provide effective protection from the moment of application for years thereafter. With the continuous development of substrates such as light metal alloys and with advancing surface pre-treatment technologies, suitable active agents must either be identified amongst existing materials or be newly developed. Currently, materials developers not only face challenges from chemical and material related requirements and cost considerations; they are also bound by legal conditions such as the EU REACH Regulations. It is to be expected that

chemicals restricted under REACH will become a rarity in the marketplace within the foreseeable future.

For new multicomponent systems such as coatings, two development options will then dominate: intelligent formulations, which can be prepared without synthesis of new materials, and the route using polymers, which are normally deemed not to be very harmful provided that their component monomers are not harmful.

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Properties of an ideal protective system

Newly developed and easily applied polymers for corrosion protection will have to meet very demanding specifications [2] covering four main aspects:

- » Material properties such as high purity, low toxicity, no or little colour and sufficient thermal stability;
- » Solvation properties such as low water solubility and non-acidity;
- » Mixing and rheological properties such as compatibility with all binder technologies and easy incorporation;
- » Efficiency properties such as a good long-term effect at low additive concentrations, high efficiency at pH values between 5 and 9, ability to be used as the sole inhibitor and, optionally, in combination with rust film inhibition materials.

Modelling polymer concepts for corrosion protection

Biological cell walls provide effective protection of the inside of the cells from environmental influences. Molecules involved in the formation of cell membranes are chemically unreactive, but despite this are firmly bound together at interfaces. They utilise the natural process of self-organisation of molecules in liquids and at surfaces to form closed layers with a homogeneous and well-defined thickness.

Results at a glance

» Regulations such as REACH are driving research into new and less toxic corrosion protection systems. It was theorised that non-toxic polymers could be developed which would self-assemble into thin layers and thus provide some protection against corrosion.

» The adsorption and association behaviour of prospected polymers could be optimised using computer-aided simulation. Polymeric corrosion inhibitors were then developed and successfully synthesised.

» Even thin sub-microscopic layers of physically adsorbed polymeric corrosion inhibitors have a protective effect on different metal substrates and metal pigments.

» After incorporation into various coating systems, the polymeric inhibitors also enhanced the corrosion resistance of coated metal substrates.

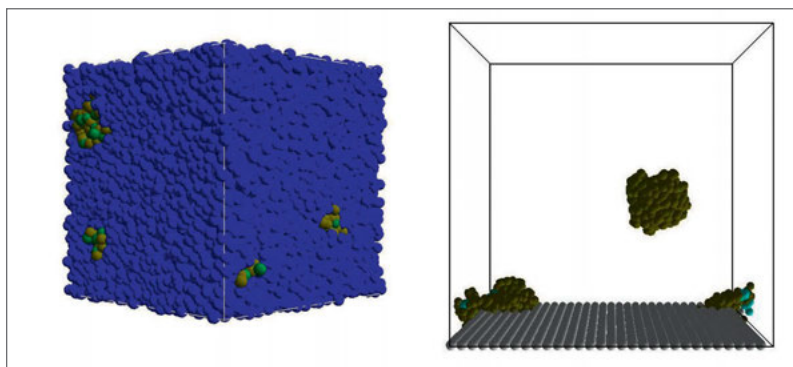


Figure 1: Simulation of the association and adsorption behaviour of polymer molecules (depicted in green tones), forming micells in a polar solvent and getting attached to a hydrophilic substrate surface (depicted in grey tones)

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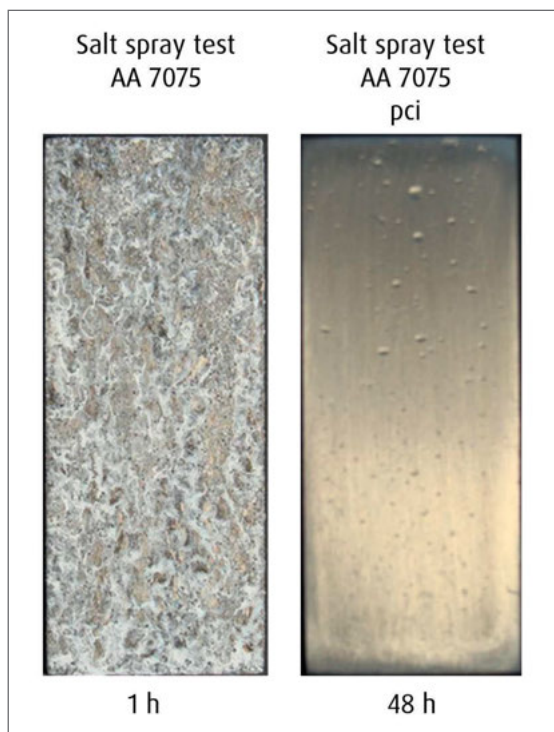


Figure 2: Corrosion protection effect of a layer of polymeric corrosion inhibitor (pci) on aluminium AA 7075

Their amphiphilic structure, that is, the combination of polar and non-polar regions in molecules, helps here. So, could double layer films made of suitable polymers protect substrates from environmental influences? Computer-aided simulation can be used to evaluate the organisation of polymers of different structure in liquid media and at substrate surfaces. In practice, prospected polymers will form highly mobile, sub-microscopic micelles in the dispersion, these micelles must undergo rapid reorganisation on contact with the substrate surface and the polymers must finally become locally attached.

Figure 1 shows the intermediate steps when modelling the association behaviour of polymer molecules in a polar solvent and their adsorption behaviour on a hydrophilic substrate surface. On the left, the solvent molecules are shown in blue, and on the right these are colourless in order to simplify the illustration and to highlight the polymers and the substrate surface shown in grey tones. Ultimately, protective layers must form which are completely closed and cover the whole substrate.

If this desired organisational process can be achieved in practice, then the simulation work will have provided valuable and time-saving information. If developers can successfully model promising polymer structures, their task is then to synthesise these and make the materials available firstly for further testing and finally for the commercial marketplace. The starting point for the chemical materials development work described below was synthesis using reactive and structural base elements to form 'head and tail' elements in polymer molecules. The relative arrangement of these units in the molecules can be customised in line with the simulation results. The chemical reactivity of the resulting molecules can be adjusted by introducing non-reactive end groups. This ensures that chemical reactions of the corrosion inhibitor molecules do not change the coating formulations or the substrate surfaces.

Polymer alone creates a protective layer

If the polymer molecules form closed layers with inherently controlled thickness on metal substrates as schematically represented in Figure 1, then this should occur when substrates are immersed in solutions or dispersions of the corrosion inhibitor. This represents a means for providing temporary corrosion protection. In an application test, ground and cleaned surfaces of sheets of aluminium alloy AA 7075 were covered with a

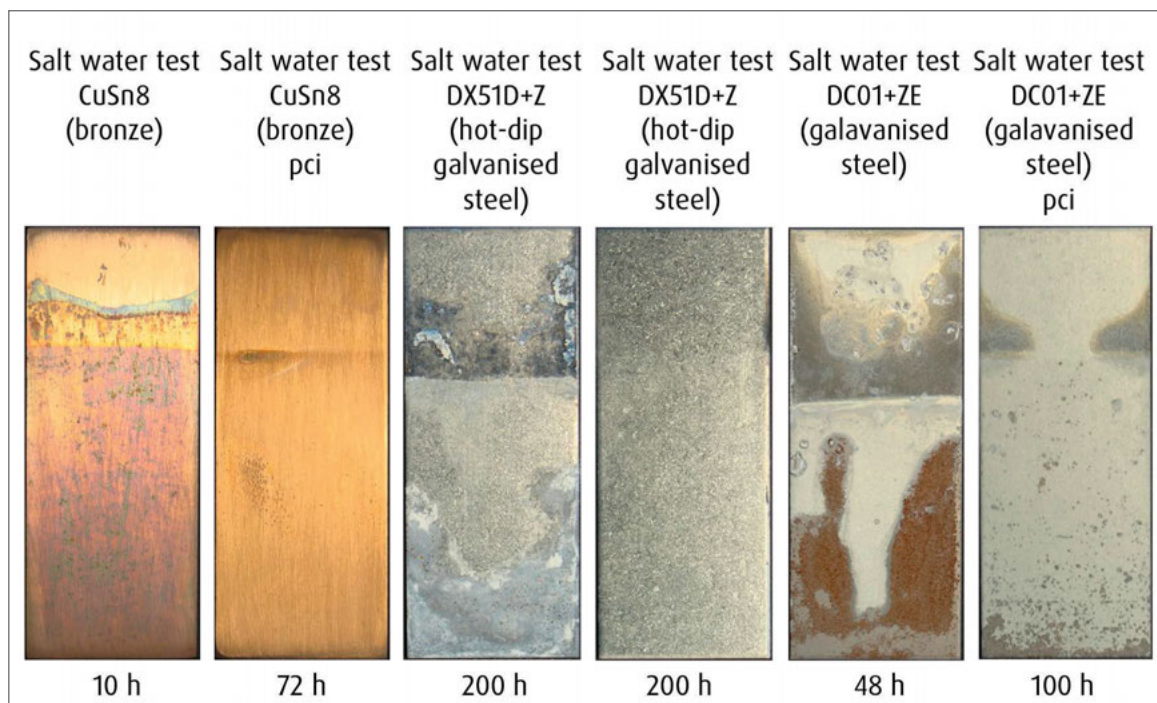


Figure 3: Corrosion protection effect of layer of a polymeric corrosion inhibitor (pci) on sheets of different metals

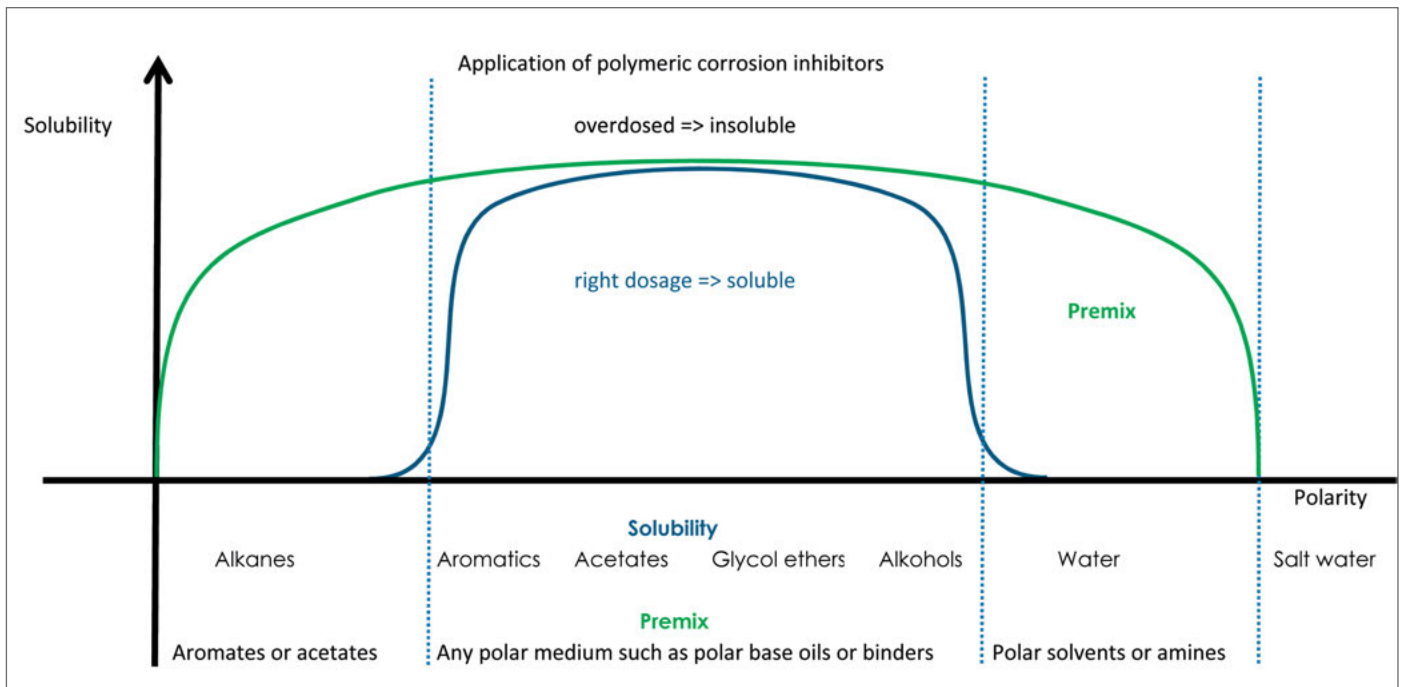


Figure 4: Solubility of polymeric corrosion inhibitors in different solvent systems improved by premixing

new polymeric corrosion inhibitor (pci) and subjected to a salt spray test. Sheets exposed to the salt spray test for 48 hours had no visual indications of corrosion (Figure 2, right), in contrast to the alloy sheets which were not protected with inhibitor, even though these were only exposed to the salt spray test for one hour (Figure 2, left).

As shown in Figure 3, the same corrosion inhibitor on bronze, hot-dip galvanised or galvanised steel sheets showed a corrosion protection effect upon immersion in 3 % aqueous sodium chloride solution, (referred to as the salt water test), for several hours. Indeed, unlike the inhibitor-free samples (the left-hand samples of the pairs of sheets in Figure 3), the inhibitor-coated samples (right-hand samples) still had a metallic brilliance after the exposure test.

More detailed examinations were made of AA 2024 sheets, applying surface analysis by X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM). These tests showed that there was a protective layer of ca. 0.01 µm thickness and that during the course of a 250 h salt spray test there was only a slight increase in the thickness of the aluminium oxide layer on the substrate. The findings that thin layers of polymeric inhibitors are effective on different substrates agrees with the mecha-

nism of physical layer formation determined from the simulation work, which did not involve adsorption at specific reactive surface sites on the oxide layers of the metal substrates.

Polymeric inhibitors are miscible with many coatings

Once the corrosion inhibiting effect of the polymers has been demonstrated, and if the chemical reactivity is low due to their chemical structure, then it may be expected that the corrosion inhibition effect will also remain intact in fluids and in cured coating systems. The effective incorporation of these typically highly viscous polymers into formulations is important here. Basically, the miscibility of the inhibitors with distinct solvent systems was evaluated and predicted by computerbased simulation. Solubility characteristics of the synthesised polymers were systematically assessed by a practical implementation in solvents of different polarity. Results are displayed in Figure 4 in a qualitative manner. The blue plot indicates the lack of solubility of the polymeric inhibitors. Compared to the green plot it becomes evident that the solubility can be improved by using premixes with low

Coating system	Coating penetration in salt spray test		Thread length in filiform test	
	Without pci ⁵	With 2 % pci ⁵	Without pci ⁵	With 2 % pci ⁵
EP (wb) ¹	after 1008 h: 6 mm	after 1008 h: 2 mm	after 504 h: 9 mm	after 504 h: 3 mm
EP (sb) ²	after 1008 h: 7 mm	after 1008 h: 2 mm	after 504 h: 12 mm	after 504 h: 3 mm
Alkyd ³	after 1008 h: 12 mm	after 1008 h: 4 mm	after 504 h: 26 mm	after 504 h: 7 mm
Alkyd-melamine ⁴	after 240 h: stopped	after 480 h: 2 mm	after 168 h: stopped	after 240 h: 5 mm

Details of test systems are as follows: 1 = Waterbased 2K epoxy system, layer thickness 85 µm; 2 = Solventbased 2K epoxy system, layer thickness 67 µm; 3 = Alkyd resin coating, oxidative drying, layer thickness 75 µm; 4 = Alkyd-melamine stoving enamel, layer thickness 78 µm; 5 = PCI is a specific polymeric corrosion inhibitor, as described in this article

Table 1: Test results for aged coating systems on aluminium sheets



Figure 5: Protective effect of polymeric corrosion inhibitors in a polyurethane coating on steel

polarity to solve it in nonpolar solvents and by using pre-mixes of polar solvents or amines to get it solved in water. For water or solvent based coatings incorporation applies accordingly.

Combining inhibitors enhances protection

For the straightforward development of novel effective and sustainable multi-component coatings, existing modern formulations will provide a reasonable base. Therefore, a deliberate effort was made to include the polymeric inhibitors in formulations containing other inhibitors such as pigments and more active flash rust inhibitors.

In this way one aim was to synchronise the timing of several corrosion protection systems in order to achieve beneficial effects, as practiced for example by *Kirmaier* [3]. Different inhibitors have differing mechanisms, which can be combined to provide optimum corrosion protection.

The inhibitor polymers were incorporated into widely differing coating systems, either in a pure form into solventbased systems or via suitable pre-mixing and formulation into waterbased systems. The resulting coating systems were applied to aluminium sheets and cured, as were coating systems without the polymeric corrosion inhibitors.

These were then subjected to a salt spray test to monitor paint detachment and to a filiform corrosion test to monitor "thread" growth. The test results are shown in *Table 1*. With a polymeric corrosion inhibitor content of two per cent there is generally less coating penetration and shorter thread lengths.

The tests indicated that there was an effective interaction between the different corrosion protection systems. Below, for example, the combined use of a polymeric corrosion inhibitor with a flash rust inhibitor is described as a protection system for steel substrates.

Standard flash rust inhibitors are salts. These are used almost exclusively in waterbased systems, (i.e. emulsions or dispersions). The addition of salts often has an

adverse effect on the properties of the formulation, and in particular on stability.

Polymeric inhibitors replace anticorrosive pigments

As flash rust inhibitors, relative to other inhibitor systems, act more quickly and in particular act during and immediately after the application of the coating, their use is often desirable. Although a slower effect would be expected for polymeric inhibitors, it is conceivable that the adsorption of polymeric inhibitors would also cover regions of the substrate already covered by the flash rust inhibitor. To study this, a 2-component solvent-based coating system was modified in various ways with inhibitors.

The test results are shown in *Figure 5*. It is clear that the use of a commercially available saltbased flash rust inhibitor alone provides no long-term protection in the salt spray test for 500 hours (see left-hand portion of the figure). A combination of 0.5 % flash rust inhibitor with 2 % of a polymeric corrosion inhibitor gives a much better result (*Figure 5, right*).

Also notable is that in these tests 10 % of corrosion protection pigment was used for the test on the left and no such pigment for the test on the right. This result suggests that polymeric inhibitors have to some extent the effect of corrosion protection pigments in coatings.

In situations where there is a limited packing density of solid particles in coating systems, it might be possible to incorporate higher quantities of other pigments than would be possible without the effect of polymeric corrosion inhibitors. The polymeric corrosion inhibitors seem to be a synergistic link between the different performance of flash rust inhibitors and corrosion protecting pigments. The interdisciplinary approach adopted here offers a promising basis for further R&D work. Combining the new polymeric corrosion inhibitors with existing inhibition agents demonstrates a beneficial interaction of the protective effects and can provide a valuable way of enhancing the surface protection of a wide variety of metallic and composite materials. ◀

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