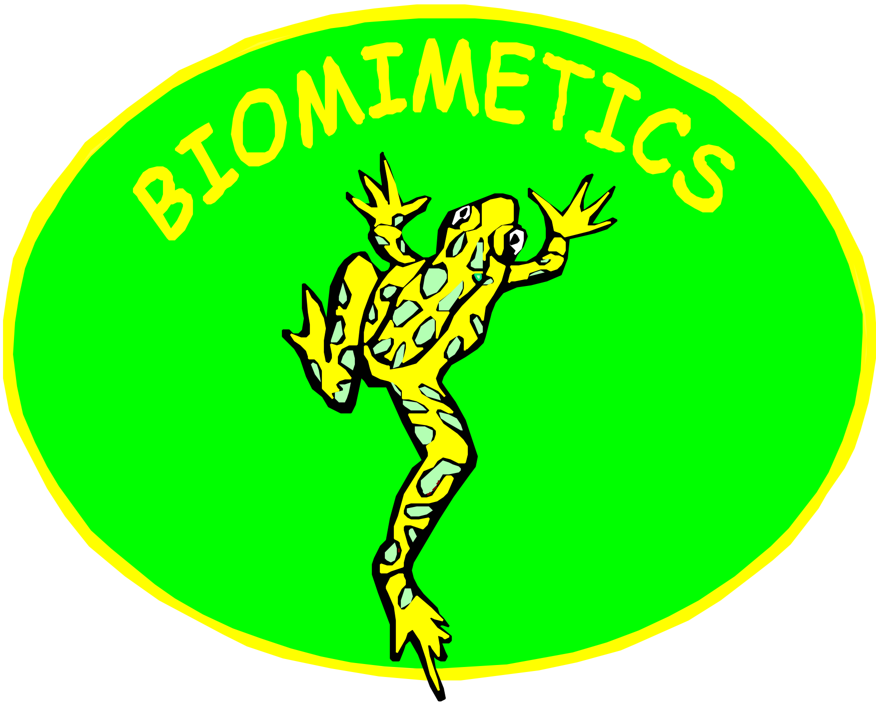
Biomimetic Coatings For Enhanced Protection Of Construction Surfaces With An Added Environmental Benefit



Executive Summary
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EXECUTIVE SUMMARY

Introduction

BICEPS is a project centred around attempts to mimic concepts found in nature in order to produce surface coatings of high structural integrity while having a minimal negative impact on the environment.

In recent times society has become increasingly aware of the need to protect the environment and to preserve natural resources. In this respect surface coatings are important, for in addition to having aesthetic value they can extend the lifetime of substrates e.g. wood, metal and ceramics, by protecting them from the adverse consequences of weathering. Nevertheless use of paints and varnishes, which have predominantly contained volatile organic solvents, themselves may have a detrimental effect on the environment.

Two features of coating technology are of particular concern to the BICEPS project. Firstly there is the issue of solvents. The majority of surface coatings are applied in a fluid state and subsequently dry to form a solid polymeric film. Typically this drying process involves loss of a liquid phase to the surroundings. Recently, under pressure to reduce potentially harmful emissions from products containing organic solvents the coatings industry has turned to formulating with water as the carrier for the resins and pigments. For both solvent and waterborne coatings it is essential that after drying the coating adheres to the substrate and becomes resistant to degrading factors in its surroundings. The structural integrity of the dry coating, its cohesion, is to an extent dependant on the nature and numbers of the chemical bonds in the polymer formed during drying. The BICEPS project aims to encourage the greater use of waterborne systems by attempting to improve the cohesion within the dry film.

The second issue of importance is that of interfacial adhesion. A primary cause of coating failure is adhesion loss at the coating — substrate interface. This leads to the environmental and commercial costs of substrate damage and re-coating. The BICEPS project aims to enhance the development of stronger substrate — coating adhesion.

The art in coating formulation is thus to create a robust product that provides not only interfacial adhesion, but also good internal cohesion which resists damage from moisture, radiation and contaminants. The natural product chemistry underlying the BICEPS study concerns a process potentially able to both improve the integrity of the coating and enhance interfacial adhesion. Evolution has encountered many requirements for strong adhesion; for example, tendon to bone, limpets to rocks. Further, there has frequently been a need to produce hard protective water impervious materials, of which fingernails and the carapace of crustacea are two of many examples. Nature has had to solve complex chemical engineering problems in order to produce such materials from small organic molecules, transported to the required site of construction in blood and sap, both essential aqueous media. At the required site living organisms employ enzymic chemistry to couple the small molecules into polymeric hydrophobic solids, or to make molecules capable of forming strong anchorage bonds.

Background

The Biocomposites Group at Southampton University have acquired knowledge and expertise in the chemistry of certain 1, 2 dihydroxy benzene derivatives, collectively known as catechols. One particular catechol Levo-dopamine (LDOPA) had been identified as a common intermediate in the formation of many naturally occurring adhesives and cements. In 1996 in collaboration with the Southampton Group, the PRA gained funding for a project to investigate the use of catechol chemistry in paint formulation.

This so named BIOMIMETIC project identified a selection of 1,2 dihydroxy benzene derivatives which were readily available, potentially chemically stable in a paint formulation, (or more particularly in the resin-latex precursor of the paint) and of suitable low toxicity. The formulation task was not easy particularly with respect to stability. In the presence of oxygen the dihydroxy benzene moiety is readily oxidised to give a mixture of 'black' quinoidal species.

It was proposed that a functional side chain could be reacted with the paint resin, leaving the dihydroxy benzene free for cross-linking or adhesive bonding. LDOPA was seen as a promising starting point for the investigation. It was suggested that the amino function of this species could be used to 'anchor' it to certain water soluble acrylic pre-polymers, which had been pre-functionalised with glycidyl methacrylate groups. In the event the research team did not find definitive evidence that the desired attachment of this catechol had been achieved. Films cast of modified resins did however harden (and darken) with time. It was suggested that some free LDOPA might be cross-linking with residual epoxide groups. Further work identified conditions under which other catechols, and possibly LDOPA, seemed to react with the pre-polymer resins. Indications were found that model paint films containing these 'modified' materials had improved hardness and hydrophobic characteristic. It was concluded that some polymeric cross-linking with the catechol was occurring, but uncertainty remained as to whether this only happened in the presence of 'excess' free catechol.

The BICEPS Project

The BICEPS objective was to build on the earlier BIOMIMETICS programme and to establish a means for providing improved performance of waterborne coatings, particularly with respect to enhanced adhesion in realistic formulations.

Potentially suitable catechols were used to modify the chemistry of a number of resins, which were subsequently incorporated into a range of laboratory-produced primers and paints. These products were applied to suitable metal or wood substrates and their weathering performance evaluated by standard laboratory and natural exposure testing. Results were interpreted with reference to the behaviour of formulations with equivalent unmodified resin. Appropriate commercial products were also used as reference standards.

During the early stages of the project a number of difficulties were found in the production of realistic model formulations from the catechol modified resins. With hindsight some of the paint/primer systems selected for use in the study were not the most appropriate. For example the water miscible resins selected in anticipation that they would show early differential results, in model coatings on steel substrate, proved too labile. Consequent very rapid degrading limited the inferences that could be drawn from the natural weathering experiments with these systems. Again, oxidative drying paints (alkyd systems) were found to be unsuited for the resin-catechol modification approach, as catechols significantly inhibited the free radical curing mechanism and the paints failed to dry. Attempts to attach of the catechol species to functional groups on the waterborne resin molecules proved challenging. While the evidence suggests that some resin-modification did take place, little further insight into the nature of this chemistry was gained during the project. At the end of the work programme there still remains a need to refine chemical procedures, to overcome potential instability problems and to optimise the level of catechol modification with respect to the formulated paint performance. The BICEPS work has indicated that at high concentrations certain catechols may actually become detrimental to weathering characteristics of paints. This could explain some of the conflicting data found in the BIOMIMETIC study, where in many of the tested systems excess catechol was present.

The BICEPS programme allowed for only a limited investigation of the relative effectiveness of different catechols on the coating's weatherability. However, in contrast to the belief at the start of the exercise, the amino functionalised catechols (e.g. dopamine and LDOPA) proved less beneficial than species, such as 3-4 dihydroxy cinnamic acid, with non-amino functionality. The rational for these observations presumably lies in the nature of the bonding of the catechol to the resin and in mode of reaction in the ultimate paint drying process.

The Conclusions

The project, while not delivering a simple formulation approach to enhancing the performance of waterborne coatings through use of catechol modified resins, has demonstrated that performance improvements are obtainable. Indications of which catechol structure is the most likely to give product improvement have been found. Limitations for the concepts, within the current state of knowledge and expertise, have been identified.

Despite collection of extensive test data, in the instances where these improved weathering performances were indicated, for products containing these modified resin, it has not been possible to determine whether the effects are due to better adhesion, improved film integrity, or to a combination of both.

Particularly important are indications, from the natural weathering experiments, that systems containing 3,4 dihydroxy cinnamic acid modified resin, on both wood and metal substrates, have a measurably improved resistance to weathering.

Overall it is concluded that, with the need for some further development work, there is a strong probability the BICEPS approach could be advantageously incorporated into commercial waterborne paint products.