Development of Formulation Guidelines for Microbial Resistant Coatings with Optimal Biocide Presence

EXECUTIVE SUMMARY

Introduction

Structural materials are frequently coated with organic surface coatings for aesthetic purposes and to afford protection from degradation in the environment. In general, given conducive conditions, typical surface coatings are intrinsically susceptible to infestation and spoilage by micro-organisms (eg. fungi such as mould and yeast). In order to provide an acceptable service life, biocidal additives are usually incorporated into the coating formulation but, by their mode of action, such additives are potentially toxic. Their use is becoming the subject of increasingly stringent regulation and restriction (eg. through the EC's Biocidal Products Directive).

There is evidence to support a view that many of the raw materials that are commonly employed in coating formulae have intrinsic effects on microbial activity of applied coatings. Some of the ingredients may support and even promote microbial spoilage of the coatings, while others may be inhibitory in their action. Currently these factors are not usually considered when designing a coating formulation with a required level of antimicrobial film protection. It is suggested that judicious selection of the raw materials should enhance the antimicrobial disposition of a paint formulation, possibly even allowing a reduction in the level of biocide while maintaining the desired level of protection.

The research contract awarded to the PRA by the DTI under its 'Degradation of Materials in Aggressive Environments, Test Method Development Programme' has permitted development of methods for evaluating the influence of raw materials on microbial activity of applied coatings. Within an experimental design framework, these methods encompassed the following areas:

- laboratory screening of films derived from simple 3-component mixtures
- laboratory & field evaluation of semi-formulated test systems
- assessment of the influence of film properties on film colonisation
- a formulation guidelines experiment
- statistical correlation of laboratory prediction studies with natural film performance.

Screening Materials for Antimicrobial Behaviour

Prior to beginning the screening tests, procurement of a wide range of raw materials for study took place. These were selected to provide representative samples from each of the generic groups of the formulation ingredients ie resins, pigments and additives. The materials were catalogued, and a list circulated to the members for comments and advice.

It was appreciated that the materials are not used in isolation, so that to find efficient and effective microbial screening procedures that were suited for investigating the activity of raw materials, an important element of the design was to provide a method allowing quantification of microbial effects for each test material in the presence of two or more of the other typical formulation components.

The range of raw materials that may be used in coating formulations is extensive. It was realised that restricting the proportion of each component to one typical concentration, while only employing three component mixtures, would still generate a requirement for a very large set of experiments. Various techniques for handling the scale of the programme were considered and it was concluded that the well established "Latin Square" experimental design would provide an efficient means for undertaking the preliminary evaluation task.

For the study, simple 3-component mixtures were prepared by dispersing pigment or extender in water, then letting down with latex. The resulting mixtures were applied to glass fibre disks, dried to form coatings, and these inoculated on agar with suspensions of either mould or yeast. Growth assessments were made at intervals up to 7 days.

Exploratory work showed the chosen technique to be capable of generating index values for the activity of each material, with respect to the effect on fungal growth response. In subsequent 9x9 Latin Square experiments (ie. giving 81 test samples in each), 99 raw materials were assessed for their influence on fungal growth using model combinations comprising a Resin, a Pigment and an Additive.

From within the experimental sets, a numerical response rating for each of the tested materials was generated. In most cases a distinction could be drawn for each material, relative to its peers, in terms of its tendency to support or to inhibit fungal growth over a fixed period of time. On this basis the materials were ranked in order of their microbial inhibitory action, for example, zinc-containing materials, many of the rutile titanium dioxides, and coalescing solvents all ranked highly in the preliminary screens.

When considering any individual rating, it is important to appreciate that in the simple screening experiment only selected combinations were examined. Furthermore, a restriction imposed by the Latin Square design is that any interaction effects are confounded, and thus were not able to be probed.

Members of the IAG expressed concerns over the possible commercial implication of assigning a specific performance rank to any raw material. The approach taken, which has commanded a wide acceptance from the raw materials suppliers, was to use the mean material rating together with its standard error in any published report. The standard errors were generally large. Thus, while the relative position of each material could be seen, the error overlap precluded the view that it was in all circumstances better than the raw material below it.

It was noted that the level of assessed microbial activity varied with time, as well as with the type of organism used in the challenge tests. The importance of the time of assessment, and its significance in determining the response index for a material was reviewed, and a 2-day or 7-day mean was selected as the measurement value for ranking purposes (the former for mould, the latter for yeast).

In response to the proposition that some raw materials may themselves contain undisclosed quantities of biocidal additives (ie. as package preservatives), experiments were carried out for which the test films were leached with water prior to inoculation. It was considered that this treatment should remove a substantial amount of any such preservative. The results of these experiments did show instances of variation in antimicrobial activity between the leached and non-leached systems.

Verification of 'Material Activity' Indices

At an early stage, it was considered necessary to test the predictive power of the material's 'activity indices' in semi-formulated model coating formulations. For this purpose, a Plackett Burman experimental design was chosen to explore the behaviour of a selection of materials when combined in a model paint formulation. This design allowed 7 factors (ie. class of materials) to be investigated in 8 experiments - although a limitation is that the materials' factors and interactions are confounded.

A representative 'typical' formulation was selected, and paints prepared. These were applied to an exterior board substrate, and the dried films exposed facing north and south at PRA's Holmbury St Mary site. The films were assessed monthly for colonisation.

In most instances, formulations showed an effect which could be predicted from a consideration of the behaviour of the ingredients in their screening tests. It was however apparent that some of the materials were displaying anomalous behaviour. These experiments uncovered other unexpected behaviour, for example, from an analysis of variance (ANOVA) the significant interaction effects of coating aspect (north- or south-facing) with the antifoam and the thickener were noted.

It is possible that the observed variations between results found during the preliminary screening experiments (laboratory-based), and those from the Plackett Burman experiment (field trial), could lie in the variations in material concentrations. It was also noted, that the fungal challenge used in the laboratory tests was limited compared to the range of organisms occurring at the exposure site at which the trials were carried out. This again may have contributed to the failure to find a strong correlation between prediction based on screening tests, and the results of the field trials.

Effect of Paint Film Properties on Fungal Growth

An important element of the investigation was concerned with the influence of the paint film properties on fungal growth. Included in this part of the study were the attempts to quantify the response to the addition of a film biocide to the paint formulations.

A Græco-Latin design was used to efficiently study the influence on colonisation of Latex, Pigment, Extender and Biocide concentration in a model formulation. The 81 paints required for the 9x9 design were prepared so that the selected 4 factors varied within a consistent general formulation. Films were applied to glass fibre disks for laboratory testing on agar, and Scots Pine sapwood panels (unpreserved) for outdoor exposure at 45°, south-facing.

Although a very low level of colonisation occurred on the panel set during the 10-month exposure, this phase of the work did indicate that judicious selection of materials can influence the microbial resistance of the paint film. There was however no indication that this resistance of the paint films outdoors could be predicted from the laboratory tests.

Of a number of surface parameters examined, 20º & 60º gloss (indicators of roughness) showed a correlation (albeit weak) with the observed spoilage. Only in one case did the programme provide a definitive indication of the biocide additive and its concentration needed to give improved film protection over that inherent in the blank system. However, the general sparse growth on these test panels makes this possibly a transient observation.

To emphasise the point, in considering the validity of the conclusions drawn from the film properties study some caution is needed, since most of the applied paint films displayed very good microbial resistance over the 10-months exposure (and consequently few growth ratings above "1" were available for analysis).

Formulation Guidelines Experiment

The work programme concluded with a full, four factor design being used to examine the effects of Pigment Volume Concentration (PVC), Latex, Biocide type, together with Biocide concentration, on the natural exposed microbial resistance of fully formulated paints.

A 'typical' paint formulation was used to generate 32 test samples containing all combinations of the 4 test factors. All had similar solids content, titanium dioxide volume concentration, and pH. Laboratory screening on agar was carried out on paints applied to glass fibre disks (leached & unleached films). Field exposure used coated Scots Pine sapwood panels (unpreserved) at 45º, south-facing.

In the first 10 months of exposure, this study showed that the unleached laboratory screening test predicted the 'better-performing' outdoor latex, and that the higher PVC systems were less susceptible to fungal growth. However, there is evidence that this latter observation may be reversing as the exposure time increases.

Another interesting observation, which is consistent with other PRA work, is that one of the film biocides tested (ie Carbendazim) effectively prevents growth of the fungus *Aureobsidium pullulans* but in the process allows other colonisation to occur. This shift in fungal ecology has given higher growth ratings than might have been anticipated at the recommended use level of the biocide.

Correlation Between Laboratory Prediction and Field Performance

At the completion of the programme a review of the results of the natural weathering experiment for formulated paints against the prediction from the various laboratory screening experiments was undertaken. The principal conclusion of this review was that the laboratory testing procedures, applied to raw materials and formulated coatings did not provide a reliable means for predicting the microbial resistance of paint films when naturally exposed.

Database

A database recording the behaviour of a range of individual materials was compiled from the results of these laboratory screening experiments. It was intended that this would be available to formulators, to assist them with the optimisation of the quantity of biocide to be used when designing coatings with a desired level of dry film antimicrobial activity.

However, it was subsequently concluded that, while the laboratory screening allowed materials to be ranked in order of antimicrobial properties, the correlation between the results from these tests on simple mixtures and those from formulations containing the materials on outdoor exposure was insufficiently strong to recommend general use of the database. Consequently, acting on the guidance of the Project's Industrial Advisory Group (IAG), a decision was taken not to release the electronic database to the industry.

Nevertheless it was concluded that if the materials were ranked on a scale "good" to "poor", then preferential selection of materials from the "good" region generally enhanced the probability that a formulation would exhibit improved dry-paint microbial resistance.

Conclusions

It is important to emphasise that, overall, the programme has shown that raw materials used in paint formulation do individually exert effects on microbial activity - with consequent potential to enhance innate film resistance.

These properties can be quantified and the material ranked for activity, by using simple screening tests. However the application of laboratory results to prediction of field performance proved to be very uncertain. As a general trend, the selection of "good" materials for use in a formulation does increase the probability that enhanced film microbial resistance will be obtained.

The effect of the film biocide is complex. On the basis of the work carried out, it is impossible to predict the optimal level or type of biocide additive that is needed to achieve a desired level of long term film protection, in formulations containing materials that have been chosen for their "good" antimicrobial properties.

An important further conclusion of the project is that, although raw materials can be placed on a scale of "good" to "poor" innate antimicrobial characteristics (ie. a measure which is dependent upon the test organism used), it is unsafe to use such ranking as a definitive guide to the material's influence on the film resistance of a paint containing it.

Also, the complexity of the behaviour, and taxa diversity, of those living organisms which are responsible for microbial spoilage of coatings, is too great to allow general use of a simplistic laboratory testing approach to either biocide optimisation, or to enhancing film protection through material selection, as was envisaged in the proposal for this project. Thus, although materials with positive inhibitory action may be selected for use, it is still necessary to undertake field testing of revised formulations to substantiate their performance outdoors in the natural environment.