

Computer-aided modelling of anti-corrosion coatings formulations

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Formulation optimisation is one of the more important steps in the development of surface coating systems. Several commercially available computer software packages that can be used to assist the formulation optimisation have been developed, provided that sufficient data are available. For systems having complex behaviour, more flexible techniques are needed. The approach that forms the basis of this paper is based on spline interpolations. Thus, the more complex behaviour of coating systems can be simulated and interpreted. The efficiency and the reliability of the models that have been developed have been evaluated using data that are relevant to anticorrosion coating systems. © 2003 Kluwer Academic Publishers

1. Introduction

When developing commercially viable surface coating formulations, it is often necessary to take several properties of the coating formulations into consideration. For instance, when developing an anticorrosion coating, the barrier properties and the flexibility of the coating systems and the adhesion of the coating to the substrate usually need to be optimised. There are several computer-aided software packages now commercially available to facilitate such optimisation. Most of these software packages employ existing statistical, analytical methods and/or neuro-network principles. As such, most of these software packages perform well when used to optimise the compositions of coating systems having relatively simple property-of-interest/composition relationship. However, often there are coating systems that have a relatively complicated property-of-interest/composition relationship. In such cases, more effective approaches to modelling are required. Guthrie and Lin [1] developed a novel approach to experimental design and to formulation modelling that was based on the spline interpolation technique. Such an approach has proven to be particularly effective when modelling complex mixture systems [2–5]. In this paper is reported the application of such mathematical modelling approach to the development of anticorrosive coating systems. The basis to this modelling approach is given below. This is then followed by application of the approach to the development of effective anticorrosion formulations.

1.1. Modelling based on spline interpolation

Establishment of mathematical models that reliably represent the relationship, between the proper-

ties/performance and the composition of the coating systems, is essential to the optimisation of surface coating formulations. A general form of such mathematical model is given as Equation 1 below.

$$Y_i = f_i(X_1, X_2, \dots, X_n) \quad (1)$$

Here, Y_i ($i = 1, 2, \dots, m$) denotes the properties of the coating system, m being the total number of property-of-interest. As indicated by Equation 1, such properties are dependent *only* on the composition (in terms of percentage or fraction) of the coating system, i.e. X_j ($j = 1, 2, \dots, n$), n being the total number of the components in the coating system. Clearly, the sum of the X 's is always 100% in terms of percentage or 1 in terms of fraction.

Several models based on *single* polynomial interpolation have been widely used in modelling mixture systems. Some of these models are given as Equations 2–7.

$$\text{Model 1: } Y = a_0 + \dots + a_i X_i \quad (2)$$

$$\text{Model 2: } Y = a_i X_i + \dots + a_{ij} X_i X_j \quad (3)$$

$$\text{Model 3: } Y = a_0 + \dots + a_i X_i + \dots + a_{ij} X_i X_j \quad (4)$$

$$\text{Model 4: } Y = a_i X_i + \dots + a_{ij} X_i X_j + \dots + a_{ijk} X_i X_j X_k \quad (5)$$

$$\text{Model 5: } Y = a_0 + \dots + a_i X_i + \dots + a_{ij} X_i X_j + \dots + a_{ijk} X_i X_j X_k \quad (6)$$

$$\text{Model 6: } Y = a_0 + \dots + a_i X_i + \dots + a_{ii} X_i^2 + \dots + a_{ij} X_i X_j + \dots + a_{ijk} X_i X_j X_k \quad (7)$$

where a_0 , a_i , a_{ij} and a_{ijk} are constants which are dependent on the characteristics of individual mixture systems; $i, j, k = 1, 2, \dots, n$ correspond to components 1, 2, \dots, n . The best model, in terms of both the convenience of data handling and the accuracy of the approximation, is Model 4. For two component mixture systems, this model can be expressed as,

$$Y = a_1X_1 + a_2X_2 + a_{12}X_1X_2 \quad (8)$$

Here, we have three constants, a_1 , a_2 , and a_{12} , represent the characteristics of an individual mixture system. It should be emphasised that all of the above models assume that the property developed is not dependent on the sequence of mixing of the components.

Most of the conventional single polynomial models, i.e. Models 1–6, can be used to simulate satisfacto-

rily the relationship between performance/property-of-interest and the composition of surface coating systems having simple behavioural features, such as those shown in Fig. 1. However, most of the conventional single polynomial models are unable to simulate the complex relationship between the properties-of-interest and the composition of the mixture, such as those represented in Fig. 2. In both Figs 1 and 2, the vertical-axis represents the property-of-interest while the other axes represent the coating compositions.

Thus, our interests lie in the application of *piecewise* polynomials as a universal model for the simulation of the property-of-interest curve/surface/space of surface coating systems.

This *piecewise* polynomial model should possess continuity and flexibility over the entire composition range, i.e. from $X_i = 0$ (or 0%) to $X_i = 1$ (or 100%),

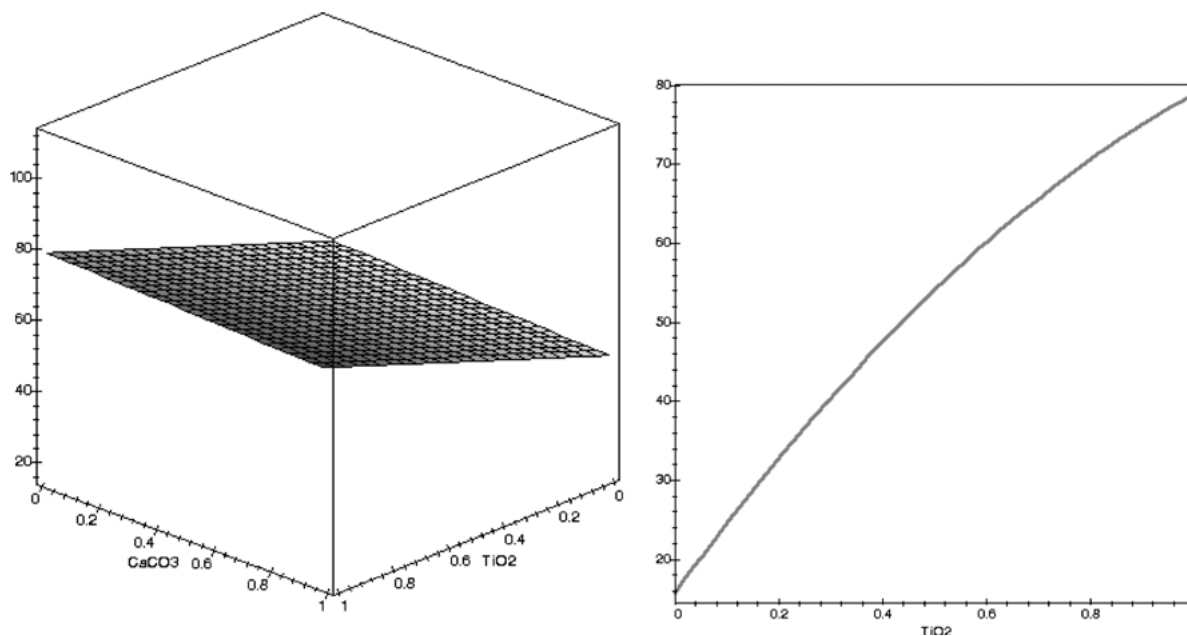


Figure 1 Typical simplistic property of interest/composition relationship.

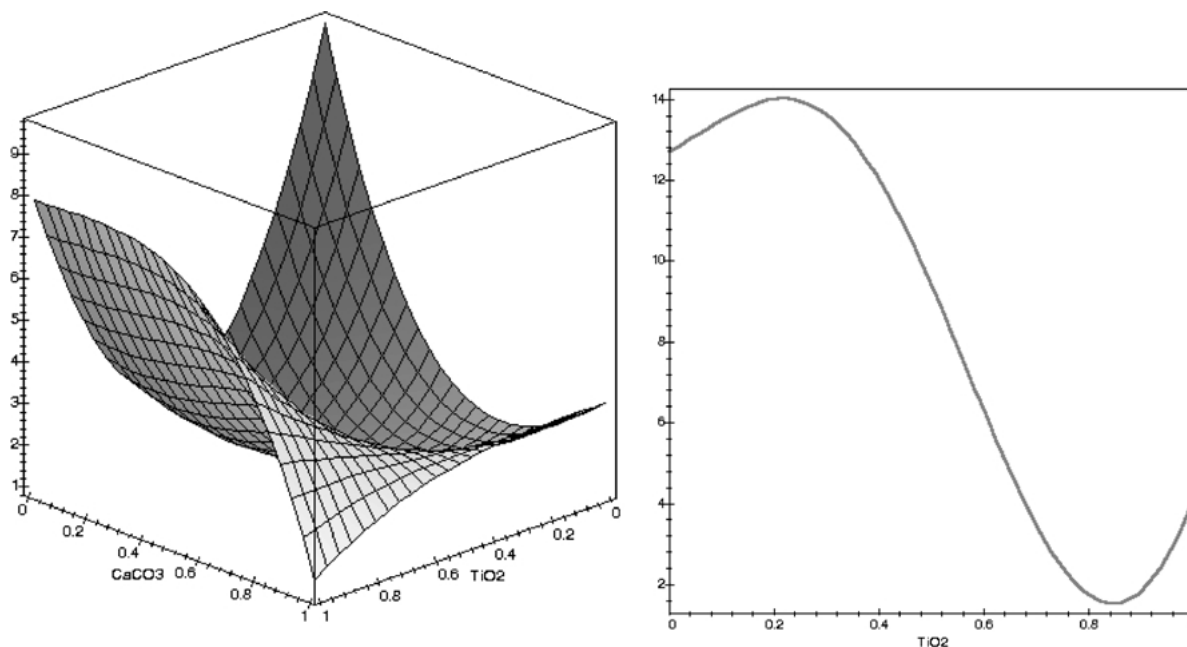


Figure 2 Typical complex property of interest/composition relationship.

$i = 1, 2, \dots, n$, cubic spline interpolation being the one that is more suitable.

The adaptation of the concept of cubic spline interpolation to the simulation of a property-of-interest curve is given as follows. Taking into account N measurements for a two component mixture, where $X_2 = 1 - X_1$, the mathematical representation of the property-of-interest curve is given as

$$Y \cap Y_{i(1)} = a_{i(1)} + b_{i(1)}(X_1 - X_{i(1)}) + c_{i(1)}(X_1 - X_{i(1)})^2 + d_{i(1)}(X_1 - X_{i(1)})^3 \quad (9)$$

where $i = 1, 2, \dots, N - 1$. Given any number of measurements, as required by the precision needed to represent the property-of-interest data, a set of splines, interpolating the property of interest curve, can be established. A spline simulation of the property-of-interest space of a p -component coating system, taking into account of $(N_1 + 1)(N_2 + 1) \dots (N_p + 1)$ measurements, can be given as

$$Y \cap Y_{i(1)} \times Y_{i(2)} \times \dots \times Y_{i(p-1)} \quad (10)$$

while,

$$Y_{i(1)} = a_{i(1)} + b_{i(1)}(X_1 - X_{i(1)}) + c_{i(1)}(X_1 - X_{i(1)})^2 + d_{i(1)}(X_1 - X_{i(1)})^3, \quad (11)$$

$$Y_{i(2)} = a_{i(2)} + b_{i(2)}(X_2 - X_{i(2)}) + c_{i(2)}(X_2 - X_{i(2)})^2 + d_{i(2)}(X_2 - X_{i(2)})^3, \quad (12)$$

and so on to

$$Y_{i(p-1)} = a_{i(p-1)} + b_{i(p-1)}(X_{p-1} - X_{i(p-1)}) + c_{i(p-1)}(X_{p-1} - X_{i(p-1)})^2 + d_{i(p-1)}(X_{p-1} - X_{i(p-1)})^3 \quad (13)$$

where, $i_{(1)} = 1, 2, \dots, N_1$; $i_{(2)} = 1, 2, \dots, N_2$; \dots ; $i_{(p-1)} = 1, 2, \dots, N_{p-1}$; N_1, N_2, \dots, N_{p-1} represent the number of coating formulations containing a different fraction of component 1, 2, $\dots, p - 1$. Terms in Y and X have the same meaning as defined previously. The evaluation of the coefficients of these splines is no more difficult than that which pertains to the case of two component mixtures.

1.2. Anticorrosive coating systems

The major coating property of concern in this study was that of anticorrosion. Anticorrosion properties are dependent on a number of other properties such as the barrier properties, the mechanical properties and the ageing properties. Thus, anticorrosion properties are demonstrated through the coating's ability to resist corrosive environments such as moisture, salt water, electrolytes, extreme temperatures, organic solvents, micro-organisms and mechanical strain.

The barrier properties of a coating are mainly attributed to the degree of crosslinking in the film-formers. In this sense, a completely impermeable coating would be ideal for anticorrosion purposes. However, in reality, such coatings would normally have poor mechanical properties such as poor flexibility and brittleness. Thus, one of the coating developer's tasks is to achieve a balance between the coating's impermeability to invasive substances and the coating's mechanical properties.

The mechanical performance of coatings is demonstrated through the coating's hardness and the coating's flexibility. While coating hardness is dependent on the degree of crosslinkage of the polymeric chains, the coating flexibility is closely related to the intrinsic characteristics of individual polymer chains. Since the process of substrate corrosion starts with the penetration of the invasive medium through the coating layer, any pits or cracks in the coating layer would reduce the anticorrosion properties of the coating layer. Therefore, the coating hardness and the coating flexibility need to be adequate to ensure a long service life.

Development of a complete coating system involves several stages. Coating development usually starts with the synthesis of the core-resin precursors. This is followed by blending the core-resin precursors with pigments and assistant polymeric species to give a complete coating system. The composition of the final coating formulation determines the performance of the coating. Optimisation of coating formulation is an inevitable development of coating systems, especially of novel coating systems.

2. Materials and equipment

A complete anticorrosion coating formulation typically consists of *at least* one core resin precursor, one assistance resin precursor and one pigment. In this study, a previously developed porphyrinogenic polymer was used as the core resin precursor. For details of the porphyrinogenic polymer, please refer to US patent US05360884 [6]. A UCB Ebecryl 600 epoxy resin precursor (supplied by UCB Chemical Sector, Speciality Chemicals Division, Drogenbos, Belgium) and a Ciba-Geigy XH943 aliphatic polyamide resin precursor (supplied by Ciba-Geigy Plastics Ltd., Duxford, Cambridge, UK) were used as the assistant resin precursors. Various pigments were used though the major emphasis was placed on the iron oxides. Two types of iron oxides were employed, namely the red oxide and the yellow oxide both of which were provided by the Kalon Group Plc., Birstall, U.K. Galvanised steel sheets (50 mm \times 100 mm), supplied by Ford Motor Company, Dagenham, were used in preparation of test panels for the study reported here.

3. Experimental procedures

In order to optimise the anticorrosive properties of the porphyrinogenic coating system. Coating formulations containing porphyrinogenic resin precursor (40%, w/w), Ebecryl 600 resin precursor (25%, w/w),

Ciba-Geigy XH 943 (8%, w/w), butanol (8%, w/w), FeO + Fe₂O₃ (17%, w/w) (FeO/Fe₂O₃ ratio varied) and other additives (2%) were prepared. In this paper is reported *only* the processes involved in optimisation of the ratio of FeO to Fe₂O₃ total amount of FeO and Fe₂O₃, the amount of other coating ingredients being unchanged, as given above.

The coating formulations, containing various amounts of FeO and Fe₂O₃, were applied onto galvanised steel test panels and cured, in a thermal oven, at 260°C for 60 seconds. The dry coating film thickness was 25 μm in all cases. The cured, coated panels were subjected to various laboratory tests. The coating formulations and the test procedure are detailed as follows.

3.1. Preparation of coating formulations for the optimisation of the pigment contents

Various experiments were designed and conducted in order to provide data for the optimisation of the ratio of FeO to Fe₂O₃ in the paint formulations. In this investigation, the emphasis has been on the optimisation of the ratio of two major pigments used in the anticorrosion coating formulations. As such, the ratio of the total amount of iron oxides to the total amount of other coating ingredients was deliberately kept constant, i.e. 17% (w/w, of the total coating formulation). The ratio of FeO to Fe₂O₃ was varied to give a series of coating formulations. A total of seven coating formulations were designed and prepared. The compositions of these coating systems, in terms of the FeO/Fe₂O₃ ratio are given in Table I.

3.2. Test procedures

As mentioned above, several mechanical properties of coating film are related to anticorrosion performance of the coating film. These mechanical properties of interest are the hardness of the coating film, the flexibility of the coating film and the adhesion of the coating film to metallic substrate. These mechanical properties, together with the anticorrosion properties, i.e. the coating's resistance to a simulated marine corrosion environment and the coating's resistance to organic solvents, of the various coating systems were acquired experimentally. Test procedures for the

acquisition of each of these properties are briefly described as follows.

3.2.1. Hardness test procedure—scratch resistance test

A scratch resistance test was used, in this study, to evaluate the hardness of the coatings. A pencil hardness tester is the most widely used instrument for the evaluation of coating hardness [7]. However, to conform to the specific requirements associated with this study, a standard metal probe, was used in the measurement of coating hardness. The edge of the probe was drawn across the coating surface. The coating was considered to have failed the hardness test when the whole or a part of the coating was removed.

3.2.2. T-bend test procedure

One of the important properties of a coating is the degree of adhesion of the coating to the substrate surface. Good adhesion contributes significantly to good anti-corrosion properties. In this study, the degree of coating adhesion to the substrate surface was evaluated using T-bend tests adapted from American Standard of Test Methods, D522-93a [8].

In a T-bend test, each coated and cured test panel was bent, as far as possible, towards the side of the bare substrate surface, as shown in Fig. 3.

A piece of standard adhesion test tape was then attached to the coated side of the corner of the test panel. Good contact between the coating surface and the tape was ensured. The tape was then pulled off the coating surface. If no coating was observed on the tape, then it is said that the coating had a flexibility measure of 0T.

If coating was observed on the tape, then the test-panel was bent again towards the bare substrate side as far as possible, as shown as Fig. 4. Again, a piece of tape was attached onto the corner of the coated side of the test panel. Good adhesion between the tape and the coating was achieved before detachment of the tape from the surface of the test panel. If no coating was observed on the tape then it was said that the coating has a flexibility of 1T. Otherwise, the procedure was repeated until no coating was observed on the tape.

TABLE I Composition ratio of FeO/Fe₂O₃ in coating samples prepared for the optimisation of FeO/Fe₂O₃ content

Sample code	Ratio	
	FeO	Fe ₂ O ₃
1	100	0
2	75	25
3	66.6	33.3
4	50	50
5	33.3	66.6
6	25	75
7	0	100

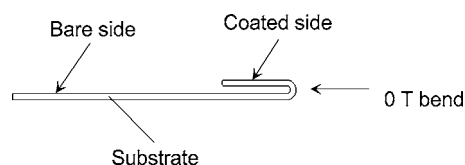


Figure 3 T-bend test (0T).

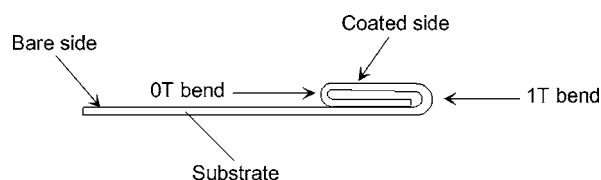


Figure 4 T-bend test (1T).

3.2.3. MEK dry rub test procedure—solvent resistance test

The solvent resistance test was designed to evaluate the coating's resistance to organic solvents. In some cases, the solvent resistance tests were used to evaluate the completeness of curing, since uncured resin precursors more easily dissolve in the solvents.

The procedure of solvent resistance assessment was adapted from American Standard of Test Methods: D5042-93 [9] and is as follows:

- (i) A piece of white tissue, folded to around 4 cm² and held in a pair of tweezers, was dipped into a chosen organic solvent.
- (ii) When withdrawn, the excess solvent was shaken from the tissue.
- (iii) The solvent-soaked tissue was rubbed against the coating surface in a standard manner.
- (iv) The number of rubbings was counted. A forward and a backward rub were counted as one complete rub. The number of rubbings needed to provide colour on the tissue was recorded. The higher the number, the better was the coating resistance to organic solvents.

To conform to the industrial requirements, methyl ethyl ketone (MEK) was used as the stripping solvent in the solvent resistance tests.

3.2.4. Salt spray test procedure

Saline resistance is one of the major anticorrosive properties. All the salt spray tests were carried out using a salt-spray unit in Materials Laboratory 13/100, Research & Engineering Centre, Ford Motor Company Limited, Laindon, Basildon, Essex, U.K. The salt spray corrosion test cabinet conditions conformed to the ASTM B117. The Ford Laboratory Test Method FLTMEU BI 103-1 was used throughout the tests.

4. Results and discussions

The hardness (scratch resistance test), the flexibility (T-bend test) and the solvent resistance (MEK dry rub) of the cured coating samples were characterised using the procedures described above. The results, together with the relevant normalised values (details following), are detailed as Table II.

The results shown in the "Observation" columns in Table II were subjected to analysis using the EXPERT computer software [2]. The EXPERT package is capable of simulating the experimental data using the conventional single polynomial models and the step-wise, multiple spline interpolation models. Since the computation programme requires that each property be represented as a numerical value, the observed coating hardness values were converted into numerical values. For

TABLE II The properties of the cured coatings

Sample code	Hardness		T-bend		MEK dry rub	
	Observation	Normalised value	Observation	Normalised value	Observation (D.R. times)	Normalised value
1	Good	1	2T-3T	0.375	30	0.6
2	Good	1	2T	0.5	30	0.6
3	Poor	0	4T	0	20	0.4
4	Good	1	3T	0.25	30	0.6
5	Fair	0.33	3T	0.25	30	0.6
6	Fair	0.33	2T	0.5	20	0.4
7*	poor	0	4T	0	20	0.4

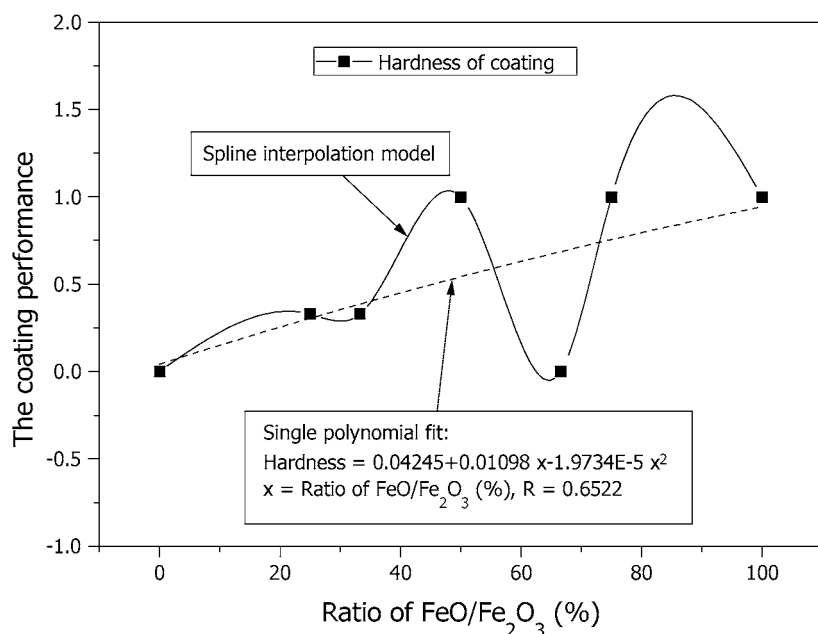


Figure 5 Modelling of hardness/composition relationship using single polynomial and spline interpolation.

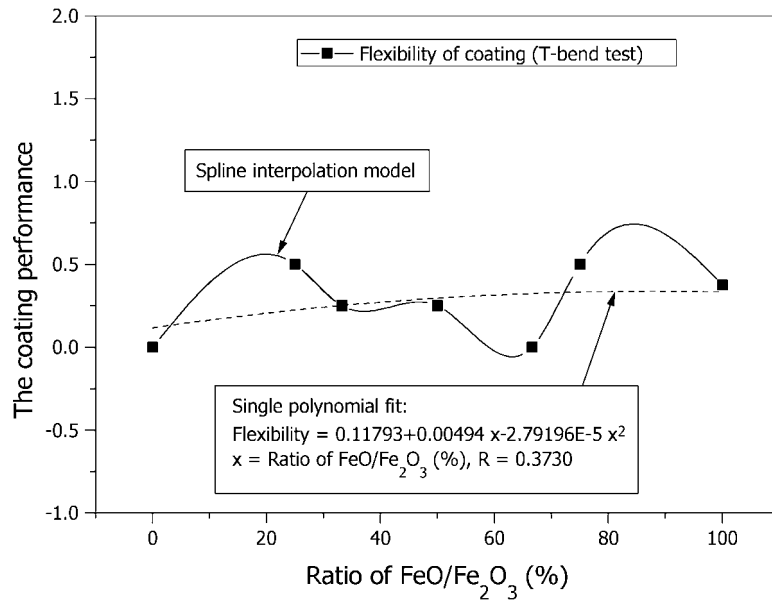


Figure 6 Modelling of flexibility/composition relationship using single polynomial and spline interpolation.

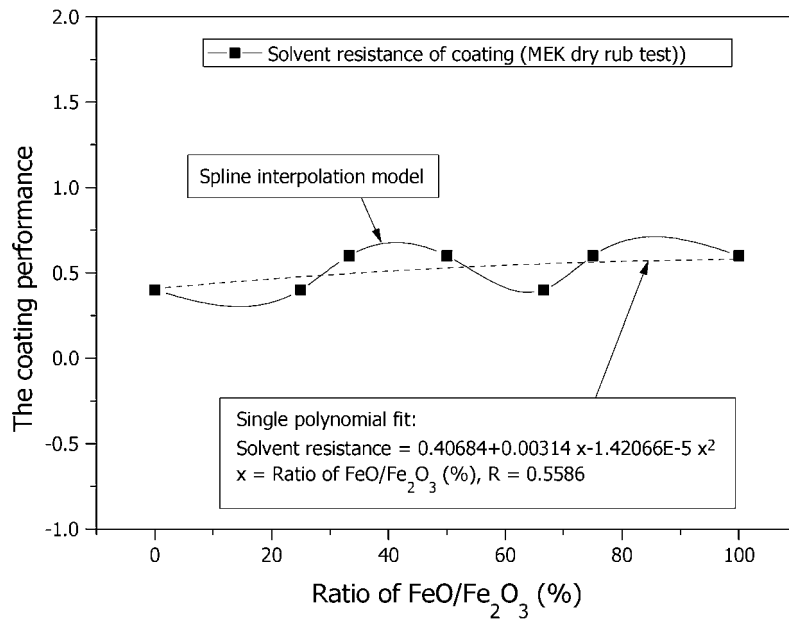


Figure 7 Modelling of solvent resistance/composition relationship using single polynomial and spline interpolation.

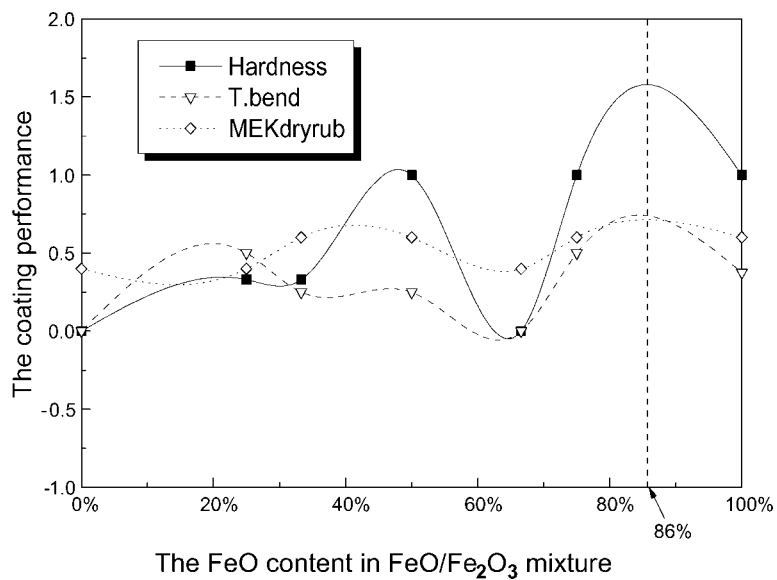


Figure 8 The prediction of optimum FeO/Fe₂O₃ composition.

the convenience of numerical processing, all results of observations were converted into fractions, i.e. values between 0.0 and 1.0. For instance, the expected coating performance, in terms of the solvent resistance, was

TABLE III Results of salt spray tests of the coated assemblies coded 1–8

Sample code	Observation
1	100 hours: White corrosion products and blisters (0.5 mm–1 mm, diameter) on edge of panel. 192 hours: Coating detached from the blister area. (maximum diameter about 0.5 mm) 480 hours: Coating detached from the blister area. (4 mm–6 mm, diameter) 600 hours: Coating detached from the blister area. (6 mm–7 mm, diameter)
2	100 hours: White corrosion products and blisters (0.5 mm–1 mm, diameter) on edge of panel. 192 hours: Coating detached from the blister area. (maximum diameter about 1 mm) 480 hours: Coating detached from the blister area. (3 mm–5 mm, diameter) 600 hours: Coating detached from the blister area. (5 mm–6 mm, diameter)
3	100 hours: White corrosion products and blisters (1 mm–2 mm, diameter) on edge of panel. 192 hours: Coating detached from the blister area. (maximum diameter about 2 mm) 480 hours: Coating detached from the blister area. (5 mm–6 mm, diameter) 600 hours: Coating detached from the blister area. (7 mm–8 mm, diameter)
4	100 hours: White corrosion products and blisters (1.5 mm–2 mm, diameter) on edge of panel. 192 hours: Coating detached from the blister area. (maximum diameter about 2 mm) 480 hours: Coating detached from the blister area. (5 mm–6 mm, diameter) 600 hours: Coating detached from the blister area. (7 mm–7.7 mm, diameter)
5	100 hours: White corrosion products and blisters (1 mm–2 mm, diameter) on edge of panel. 192 hours: Coating detached from the blister area. (maximum diameter about 1.5 mm) 480 hours: Coating detached from the blister area. (5 mm–6 mm, diameter) 600 hours: Coating detached from the blister area. (7 mm–8 mm, diameter)
6	100 hours: White corrosion products and blisters (0.1 mm–0.5 mm, diameter) on edge of panel. 192 hours: Coating detached from the blister area. (maximum diameter about 0.3 mm) 480 hours: Coating detached from the blister area. (3 mm–4 mm, diameter) 600 hours: Coating detached from the blister area. (5 mm–6 mm, diameter)
7	100 hours: White corrosion products and blisters (0.2 mm–1 mm, diameter) on edge of panel. 192 hours: Coating detached from the blister area. (maximum diameter about 0.5 mm) 480 hours: Coating detached from the blister area. (3 mm–4 mm, diameter) 600 hours: Coating detached from the blister area. (5 mm–6 mm, diameter)
8	192 hours: White corrosion products on edge of panel. 360 hours: Several blisters on the edge. (1 mm–1.5 mm, diameter) 480 hours: Coating detached from the blister area. (1.5 mm–2 mm, diameter) 600 hours: Coating detached from the blister area. (3 mm–3.5 mm, diameter)

50 MEK double rubs. Therefore, the 50 times of MEK double rub was set at the value of 1.0. Consequently, the MEK double rub property of the coating sample No. 2, which resisted 30 MEK double rubs was considered to be 0.6, i.e. $\frac{30}{50} = 0.6$, in a 0–1 scale. The settings for the hardness were standardised as good = 1.0; fair = 0.66; intermediate = 0.33; and poor = 0.0. Similarly, the settings for the coating adhesion properties were 0T = 1.0; 2T = 0.5; and 4T = 0.0 and so on.

The normalised/standardised values of the coating properties were then input to the computation programme, EXPERT, with which mathematical simulations were generated for each of the properties-of-interest, i.e. the coating's hardness, the coating's flexibility and the coating's solvent resistance. The relationships between the coating's properties-of-interest and the FeO/Fe₂O₃ composition are shown as Figs 5–7. The solid square symbols, in Figs 5–7, represent the normalised, average observation values. The dashed curves represent the simulation of the experimental data using a single polynomial model. The solid curves represent the simulation/predictions by spline-based models.

It can be seen, from Figs 5–7, that models based on spline interpolation give much improved simulation of the experimental data in all cases, compared to the models based on a single polynomial. Indeed, models based on single polynomial gave very poor simulation of the experimental data, coefficients of regression being 0.6522 (hardness), 0.3730 (flexibility) and 0.5586 (solvent resistance).

The EXPERT software further predicted the compositions of FeO/Fe₂O₃ in the coating formulations that would give the optimal hardness, the optimal adhesion and the optimal solvent resistance. These were 86% FeO/14% Fe₂O₃ for optimal hardness, 86% FeO/14% Fe₂O₃ for optimal adhesion (T-bend) and 86% FeO/14% Fe₂O₃ for optimal solvent resistance, total amount of FeO/Fe₂O₃ being 17% of the total coating formulation. (See Fig. 8)

In order to verify the reliability of such prediction, a coating formulation containing FeO and Fe₂O₃ to the ratio 86% to 14% (the total amount of FeO/Fe₂O₃ constituting 17% of the total coating formulation) was prepared. This coating formulation was coated onto galvanised steel panels and cured in a preheated oven, at 260°C for one minute. This coating sample is denoted as Sample 8. The coating properties were measured

TABLE IV Average diameter of blisters on coating tested by salt spray

Sample code	Length of salt spray test (hr.) FeO/Fe ₂ O ₃ (%)	Average diameter of blisters on coating (mm)			
		100	192	480	600
8	0	0.5	0.5	3.5	5.5
7	25	0.3	0.3	3.5	5.5
6	33.3	1.5	1.5	5.5	7.5
5	50	1.75	2	5.5	7.35
4	66.6	1.5	2	5.5	7.5
3	75	0.75	1	4	5.5
2	86	0	0	1.75	3.25
1	100	0.5	0.5	5	6.5

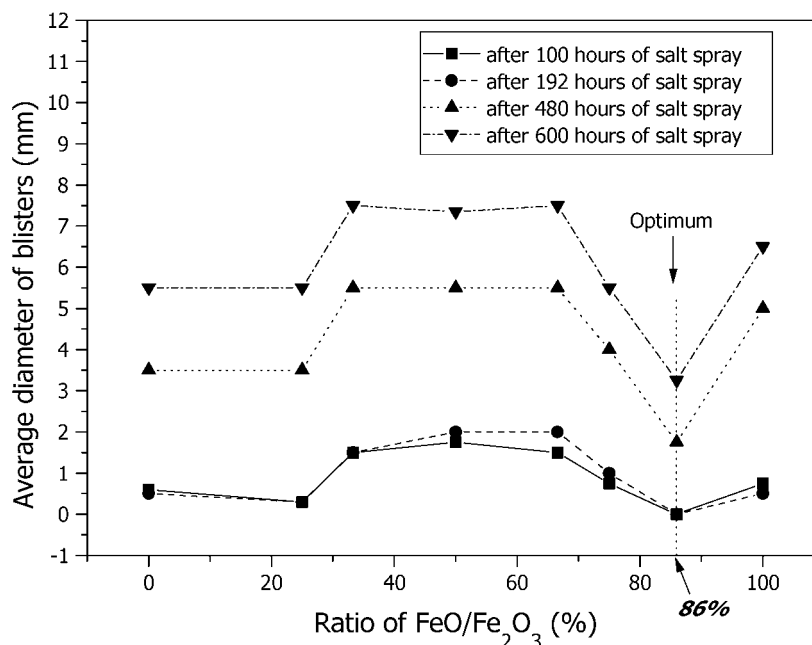


Figure 9 Results of salt spray test.

as hardness = Excellent, T-bend = 0T and MEK dry rub = 35. These values agree very well with the predicted optimum values as indicated in Fig. 8.

Galvanised test panels, coated with the coating formulations containing various amount of FeO and of Fe₂O₃, i.e. Samples 1–8, were subjected to salt spray tests. The results of these salt spray tests are detailed in Table III.

The average diameter of the blisters on the coating observed, for each test panel, at various stages of the salt spray test, is recorded in Table IV. The same data are graphically presented in Fig. 9.

It can be seen, from Table IV and from Fig. 9, that Sample 9, i.e. coating formulation containing the predicted optimal quantity of FeO/Fe₂O₃, gave the best anticorrosion performance. This indicates that 86%:14% (FeO/Fe₂O₃) was the optimal composition. Thus, the reliability of the prediction by the model based on spline interpolation was confirmed.

It was therefore clear that an optimal porphyrinogenic anticorrosion coating formulation would consist of 40% of porphyrinogenic resin precursor, 25% of Ebecryl 600, 8% of XH943, 8% butanol, 14.62% FeO, 2.38% Fe₂O₃ and 2% other additives.

5. Conclusions

It can be concluded from the above that the model based on spline interpolation provides a uniquely efficient solution to the modelling of the properties-of-

interest/compositions relationship of coating systems showing complicated behaviour. Indeed, using such model, a high degree of simulation of the experimental data can be achieved.

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