

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

**Diffusion and Uptake of Moisture through Paint Films  
Leading to Corrosion of Metal Substrates:  
A Diffusion - Adsorption Model with Reaction.**

A thesis presented in partial fulfilment of  
the requirements for the degree of  
Doctor of Philosophy  
in Mathematics at  
Massey University

Antony K Van Dyk  
1996

**ABSTRACT-**

Corrosion occurs in response to the availability of water, oxygen and other agents at metal surfaces. The rate of corrosion depends critically upon the concentrations of these agents. At a metal surface protected by a paint layer, these concentrations are governed by diffusion through the paint film and by adsorption onto the metal surface in competition with polymer molecules of the adherent paint film. A mathematical model is developed for this problem and its behaviour and evolution in time is analysed.

The conceptual basis of this model is different from others in that it combines equations of diffusive processes with equations of paint film adherence (competitive adsorption) at the metal surface. The corrosion process is considered to arise through boundary conditions for the diffusion equations with rates governed by variables described in the competitive adsorption equations. The nonlinearity of these competitive adsorption equations is the key to describing long periods of protective action provided by paint films, with negligible corrosion of the metal substrate, followed by the sudden onset of rapidly accelerating corrosion and the consequent accumulation of corrosion product (rust). Concomitant loss of competitive adsorption (adhesion) by the paint film is a typical end result.

Electrochemical activity of the metal substrate is evaluated as a corrosion current. This is determined by concentrations of water and oxygen in the internal environment, and by chemical activity in the adsorbed layer. The mechanism of corrosion of a painted metal surface is theorised to occur through active sites not covered by adsorbed polymer, water or oxygen.

Numerical simulations were done using a detailed computer algorithm developed specifically for this purpose. These simulations give insight into the model's behaviour and aid determination of simplified constitutive relationships which lead to a simplified model which allows easy determination of the thresholds for the onset of rapid corrosion.

It turns out that the diffusion of water and oxygen through the paint film is normally very quick. The rate determining step is directly related to the competition between water, oxygen and coating polymer adherent to the metal surface, and coating polymer adherent to corrosion product. Once zinc (or any other metal) ions approach saturation in solution at the metal surface, the coating polymer approaches saturation with zinc and loses competitive adsorption onto the metal surface. Crystallinity of the adsorbed polymer declines and chemical activity coefficients in the adsorbed layer are reduced. Concentrations of water and oxygen in the adsorbed layer increase and metal active sites are exposed. The result is a surge in the rate of corrosion leading to the rapid formation of corrosion product. This in turn leads to enhanced degradation and free corrosion of the metal surface.

## **ACKNOWLEDGEMENTS**

I would like to thank Resene Paints Limited and Tony Nightingale for support of this work, and Colin Gooch for encouragement and enthusiasm during the development of the model and exploration of its behaviour. Thanks also to Dr. Stephen White for writing the Fortran programme to numerically simulate the model.

Thanks to Professor Graeme Wake and Dr. Alex McNabb for guidance in testing the model and resolve in rejecting many failed precursors. Thanks also for your unfailing optimism that a plausible model would be found.

Finally I would like to thank my wife Carmela and family for their patience and understanding.

Note: While not referred to specifically in the text we have made general use of the following texts: Birkhoff and Rota (1962); Cesari (1963); Lefschetz (1959); Murray (1974); Roberts and Kaufman (1966); Sperb (1981); and Verhulst (1963)

## CONTENTS

1.	Introduction	page 1
2.	Model Description	11
3.	Model Summary	50
4.	Review of Model Development	55
5.	Special Cases	81
6.	Numerical Modelling	92
7.	Reduced Model	107
8.	Model Simplification	118
9.	Simplified Reduced Model	127
10.	Model Variations	137
11.	Concluding Remarks	150
	Appendix	153
	<i>Fortran 90 programme</i>	
	References	190

**LIST OF FIGURES**

Figure 1	page 12
Figure 2a, 2b	14
Figure 3	18
Figure 4	19
Figure 5	21
Figure 6	23
Figure 7	98
Figure 8	100
Figure 9	101
Figure 10	102
Figure 11	103
Figure 12	104
Figure 13	105
Figure 14	109
Figure 15	110
Figure 16	112
Figure 17	114
Figure 18	115
Figure 19	120
Figure 20	120

**LIST OF FIGURES continued**

Figure 21	121
Figure 22	121
Figure 23	122
Figure 24	123
Figure 25	125
Figure 26	126
Figure 27	129
Figure 28	130
Figure 29	133
Figure 30	134
Figure 31	134
Figure 32	136
Figure 33	140
Figure 34	142

**LIST OF TABLES**

Table 1	page 54
Table 2	54
Table 3	71
Table 4	96
Table 5	96
Table 6	97

<b><u>NOMENCLATURE</u></b>	pp52-54
----------------------------	---------