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

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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.

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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)

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