



The influence of reduced pressures on the film formation of cathodic electrodeposition paints



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ABSTRACT

Within the last decades, cathodic electrodeposition paints have experienced extensive economic success – most prominently in automobile body coating. However, to date, it is not possible to calculate the deposition behaviour of cathodic electrodeposition coating materials exclusively from bath and application data, since the key mechanisms responsible for the film formation are not sufficiently understood. By performing coating experiments with cathodic electrodeposition paints at reduced pressures, in this work, experimental evidence for a pressure dependent procedure of film formation is given. Supported by charge-flow and current-time plots, this fact is attributed to the influence of the pressure-dependent volumes of the generated hydrogen bubbles, thus providing new insights into the deposition behaviour of cathodic electrodeposition paints.

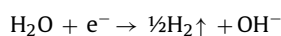
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1. Introduction

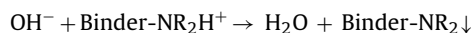
The process of coating by cathodic electrodeposition is currently the most important painting method to protect metals against corrosion. This is particularly relevant to the automotive industry, where for more than forty years nearly every car produced worldwide is primed in this way. The method is efficient, environmentally friendly and the process technology is well controlled.

Cathodic electrodeposition coating materials are aqueous and low viscosity liquids. The solvent content could be decreased from 3 to 5% in 1975 to less than 0.5% in the newest generation of cathodic electrodeposition paints [1]. During the coating process, the workpiece is immersed into the paint and operates as the cathode. Generally, amino group-containing epoxy resins neutralized with acetic acid or lactic acid are used as binders.

The coating process consists of two partial reactions: At first, the so called “primary reaction”, the electrolysis of water takes place. By this process hydrogen and an alkaline boundary layer are formed on the surface of the workpiece:



During a subsequent “secondary reaction”, the water-miscible ionic form of the binder is converted into the immiscible neutral form by reaction with the hydroxide ions of the alkaline boundary layer. Binder, crosslinker, solvents and pigments precipitate on the surface of the workpiece forming the so called “wet film”, which is usually thermally crosslinked finally.



The parameters influencing the application behaviour and the final film thickness of electrodeposition coatings have been extensively studied [2,3], particularly voltage [4,5], bath temperature [4,6], deposition time [4,7], substrate [8,9], solvent content [10], degree of neutralisation [7] and solid content [5,7]. Nevertheless, based on coating and application parameters such as bath conductivity, wet film conductivity, deposition equivalent or voltage, it is not possible to date to predict the growth of an electrodeposition coating and its final thickness with the required accuracy. Currently, only calculation methods requiring prolonged measurements of the deposition behaviour of the paints to be simulated [11–14] are available. Other approaches involve electrostatics [14–16] or computer science [14,17].

A deeper understanding of the film formation and the implementation into an improved film formation model of electrodeposition paints would be very advantageous, in particular for the automotive industry. It would be helpful to design car bodies with an optimised shape avoiding too low film thicknesses and uncoated areas.

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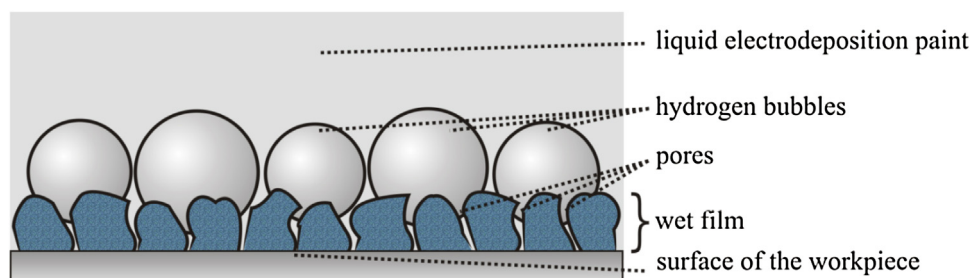


Fig. 1. Schematic illustration of the processes during the film formation of cathodic electrodeposition paints.

The difficulties in modelling the film thickness growth of electrodeposition paints are due to the complexity of the numerous processes taking place. The precipitated wet film covers the substrate surface not forming a uniform layer but being rough and porous. Electrical current flow continues to be possible and the electrolysis of water and precipitation of further wet film can go on. The hydrogen formed by the electrolysis forms bubbles, which are incorporated into the wet film or adhering to its surface, but usually do not detach (Fig. 1).

The pores should close quickly due to coalescence of the coagulated paint, but this is not the case. It is prevented by the continued formation of hydrogen, which escapes through the pores forming bubbles. This is discussed in detail in Lit. [7]. While the hydrogen bubbles start to be formed by electrolysis immediately after the application of the voltage (primary reaction), a certain period of time passes until the paint coagulation (secondary reaction) starts. Under realistic deposition conditions, this induction period is only fraction of a second [9], but due to this time difference, the pores are retained over the entire period of electrodeposition. Here, the influence of the volume of the hydrogen bubbles on the structure and properties of the wet film structure becomes particularly evident.

The instantaneous current density is thus significantly affected by the actual nature of the growing wet film. It is likely that the current mainly flows through the paint-filled pores, while the wet film and the hydrogen bubbles represent poor conductors or insulators. In addition, the wet film is first heated due to the applied electrical power and then cooled again in the further course of the deposition, which also influences the total resistance in a complicated manner. Evidently, the dynamics of such a complex process is challenging to be described mathematically.

However, the deposition process may be investigated by studying the growing film resistance in time. For that purpose, the current density is plotted as a function of time as exemplarily shown in Fig. 2 [18].

A noticeable maximum of the current density can be observed within the range 0.1–0.3 s. Here the formation of the electrical resistance starts by paint coagulation. At higher voltages, in many cases a second, flatter maximum is found after a few seconds [19,20].

Different theoretical approaches have been described in the literature for calculating the shape of the plots shown in Fig. 2. According to Machu [21], during the process of wet film deposition, the substrate surface is increasingly covered by coagulated electrodeposition paint, which is regarded as an electrical insulator. The further current flow takes place only in the part of the surface which has not yet been covered. Further consideration of geometrical, electrochemical and electrical parameters can be used to derive an exponential decrease in the current density. A further approach is based on the assumption that the layer thickness growth, viewed at any time, is proportional to the instantaneous current density [22,23]. According to this approach, the current density will decrease by $1/\sqrt{t}$. However, both models do not provide a sufficiently accurate description of reality, as it can be seen in Fig. 2. This is due to simplifying assumptions such as a homoge-

neous wet film with a smooth surface, uniformly increasing layer thickness and a constant specific wet film resistance. Interestingly, even a more sophisticated model including a porous surface and an electrically conductive deposited paint material [19] does not reveal more realistic results.

A further advanced model [24] of the film growth regards the wet film as a unity of growing inverse cones being surrounded by shrinking pores. This approach provides an equation comprising two paint-specific parameters being derived from experimentally determined current-time-plots. Thus, in the case of the investigated resin dispersions, satisfactory consistency between model and reality is obtained.

A possible explanation for the difficulties to develop adequate film building models may be the non-consideration of the insulating influence of hydrogen bubbles, increasing the resistance of the wet film and thus affecting the film formation. As can be easily calculated using Faraday's law of electrolysis, the volume of hydrogen formed is about ten times larger than that of the deposited paint on the surface of the workpiece. To date, there is no theoretical approach to calculate the layer thickness growth taking into account above mentioned influence.

Therefore, the scope of this work is to examine the influence of the volume of emerged hydrogen bubbles on the film formation of electrodeposition coatings. The only way to vary the volume of the hydrogen bubbles without influencing other deposition parameters is to carry out the coating experiments at different reduced pressures. Thus, the volume of the hydrogen bubbles can be increased mainly according to the ideal gas law. In comparison with the external pressure, the influences of the hydrostatic pressure and the Laplace pressure are small and should be disregarded.

To date, such studies have only been performed using porous steel as a substrate and with the objective to improve the corrosion protection [25,26]. The influence of the hydrogen bubbles on the deposition mechanism of cathodic electrodeposition paints has still remained unexplored. By addressing this fundamental question, the present work will provide new insights into the deposition mechanism of cathodic electrodeposition paints.

2. Materials and methods

2.1. Materials

The painting experiments were mainly carried out on phosphated steel panels, and partially on aluminium panels. Gardobond 26S phosphate steel panels were provided by Chemetall GmbH, Frankfurt am Main. Al 99.5 panels were purchased from Meyer & Co. GmbH, Iserlohn. The size of the panels was 30 mm × 100 mm. Their thickness was 0.5 mm (aluminium) respectively 1.0 mm (steel). Before use, the panels were cleaned with a solvent mixture. Fully deionized water was used throughout the work. 1-Butanol (VWR) was used as received without further purification. As cathodic electrodeposition paint, we used DELTA-eLack® 800 provided by

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