# Electrodeposition of Coatings

R. F. GOULD

ADVANCES IN CHEMISTRY SERIES 119

## Electrodeposition of Coatings

A symposium sponsored by
the Division of Organic
Coatings and Plastics
Chemistry at the 161st
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Chemical Society, Los Angeles,
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George E. F. Brewer,

Symposium Chairman

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#### **FOREWORD**

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are referred critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

#### **PREFACE**

In the late 1950's, as a consultant to Ford Motor Co., I called to the attention of my supervisor, G. L. Burnside, the concept of electrophoretic deposition of water-borne paint compositions. Soon the magnitude of this project became apparent, and our thoughts and experimentations were disclosed in confidence to some leading paint manufacturers. For me, this resulted in a most pleasant cooperation with many farsighted leaders in research and development. Indeed, at that time farsightedness was needed to embark on the project of electrodeposition of paint. Fortunately, the investigations were successful: electrodeposition is now a worldwide operation.

About two years ago, I was asked by the officers of the American Chemical Society Division of Organic Coatings and Plastics Chemistry to preside at the Symposium on Electrodeposition of Coatings at the 161st National Meeting of the American Chemical Society, March-April, 1971, in Los Angeles. The papers presented at this meeting, together with short introductory reviews of the total field, are the subject of the present volume.

Sincere thanks go to the authors of these papers for accepting my invitation to participate in this publication. Their work is published in excellent company. Beyond the authors, credit goes to their supervisors and organizations who have so generously furnished guidance and supporting services which made this volume possible. While I cannot attempt to single out all these indirect contributors in all the organizations involved, my own thanks go to G. L. Burnside, H. N. Bogart, and P. H. Ponta of Ford Motor Co., and last, but not least, to L. J. Nowacki and L. H. Princen of the American Chemical Society, Division of Organic Coatings and Plastics Chemistry.

Brighton, Mich. August 1972 George E. F. Brewer

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### Status, Process, and Equipment: Introduction

#### GEORGE E. F. BREWER

Electrophoretic migration and electrodeposition of colloidal particles have been observed as early as 1809 (1) and are described in the literature as "electrophoretic migration" and "electrophoretic deposition" of clay, waxes, asphalt, rubber, and various colloids from their dispersions in water and in organic liquids (2). For many years, it was apparently difficult to maintain bath conditions which result in continuously repeatable formation of electrodeposits; at any rate, none of these electrodeposition processes seems to have attained commercial reality.

Much work has been done in the field of electrodeposition of organic film formers from aqueous baths. At least three books on the subject have been published in the past few years (3, 4, 5). The electrodeposition of the film former is a radically new form of paint application, which, in conjunction with other operations, results in outstandingly improved corrosion protection. In developing the total process, our interest was directed toward the four major steps (see Figure 1):

- (1) Metal pretreatment
- (2) Electrodeposition
- (3) Rinse
- (4) Bake

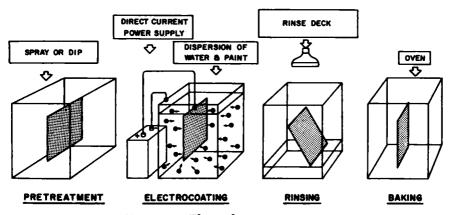


Figure 1. Electrodeposition process

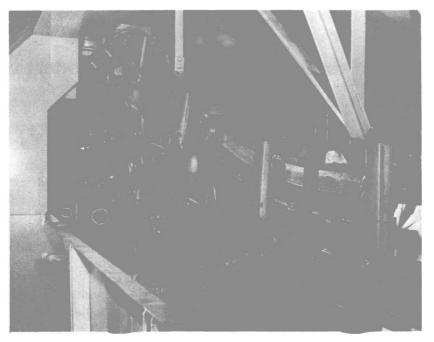


Figure 2. Typical electrocoating tank

To minimize the task of converting existing plants and equipment for electrodeposition, the process was designed to confine equipment changes to one section of the paint department. No change is normally required in the metal preparation equipment and bake oven, which exist in practically all conventional painting operations. All operations subsequent to electrodeposition—such as sanding or top coating—are carried out in a conventional manner.

Electrodepositable paints are on the market for one-coat application as primer-surfacers, etc., in all ranges of gloss and in practically all colors. In these materials, the electrical resistance of the cured coat is usually so high that no second electrocoat can be deposited over the first coat. There are, however, some electrocoating materials on the market from which coats of low electrical resistance are formed, so that a top coat can be electrodeposited (6).

#### Coating Bath Solids

Most baths contain 5-15% non-volatiles, of which the pigment-tobinder ratio seems to be rarely higher than 1 part pigment to 2 parts binder. A low non-volatile concentration in the bath is desirable since workpieces, when lifted from the bath, carry with them a certain volume of bath. Thus, the lower the bath solids, the smaller the so-called "dragout loss." Also, lower bath solid concentration results in shorter time of "dwell" in the bath, and pumping stability becomes less critical.

#### Bath Agitation and Filtration

Paint solid settling is prevented by pumps, draft tubes, line-shaft agitators, ejector nozzles, etc. Their agitational capability is sufficient to cycle the entire tank volume in 6 to 30 minutes. In addition to strainers, filters are provided with pore sizes of 5 to 75 microns. The total bath volume passes through the filter in many cases once every 30 to 120 minutes.

#### Coating Tanks

BREWER

Electrocoating tanks (Figure 2), like conventional dip tanks, are operated on either a continuous or a batch type basis. In the latter case, one piece or a number of pieces are located over the tank and then dipped into the bath. A total submersion to 6 inches below the surface with 6 inches clearance on all sides is the usual practice. The tank wall can be used as the counter electrode (Figure 3), or the tank wall can be lined

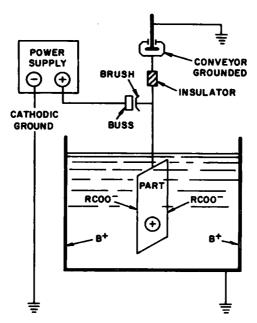


Figure 3. Solubilizer re-use (solubilizer deficient feed)

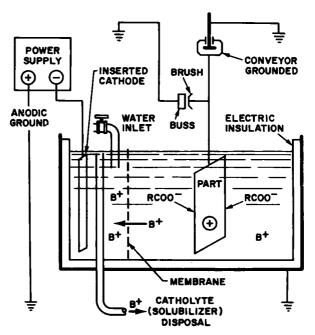


Figure 4. Solubilizer removal (completely solubilized feed)

with an electrically insulating coat (Figure 4), while the counter electrodes are inserted in the tank and then positioned according to size or shape of the workpieces. When lined tanks are used, the workpieces can be grounded through the conveyor. In many cases, however, the hanging device (paint hook) carries an electric contactor (brush) sliding along a grounded rail (buss bar) to ensure electrical ground. If the entire tank wall is used as the electrode, it forms the grounded side of the circuit. In this case, the hook on which the workpieces are hanging carries an insulating link. The lower, insulated section of the hook contacts the buss bar from which it receives the electrical energy.

#### Cooling Equipment

Practically all the electric input is converted into heat and is removed through adequately sized chillers. Constant bath temperature is usually maintained at 70°-90°F as recommended by the paint supplier.

#### Electrodeposition

Cleaned or pretreated workpieces enter the electrocoating tank either electrically energized or without electric charge (Figure 5). It is desirable

to enter workpieces into a bath at full coating voltage since snorter coating time results. However, some electrocoating baths produce streaks ("hash marks") on merchandise which is entered under full coating voltage. Un-energized or low energized pieces entered into the same bath are free from defects.

Many installations provide the option of un-energized or low energized entry through the use of two or more power sources. Multiple power sources also ensure continued, though lowered, production in case of breakdown of one power source. Amperage limitations, current cycling, or intermittent current application lengthen the required coating time since it is the applied ampere-seconds (coulombs) which produce the electrodeposit.

Current consumption ranges from about 15 coulombs/gram of finished coat up to 150 coulombs/gram, resulting in an overall requirement of 2 to 4 amp/sq ft for 1 to 3 minutes. For special work such as wires, steel bands, etc., coating times as low as 6 seconds are reported. The voltage requirement is largely dictated by the nature of the dispersed resin. Installations are usually operated between 200 and 400 volts though some are reported to operate at voltages as low as 50 volts, others as high as 1000 volts.

#### Rinse

BREWER

The electrocoated workpieces, when emerging from the coating tank, carry a well-adhering paint film, almost free from solvent or volatile matter. Bath droplets cling to these surfaces, and difficult-to-drain sections are full of coating bath. The carry out is usually rinsed off or may be reclaimed by a process such as ultrafiltration (7).

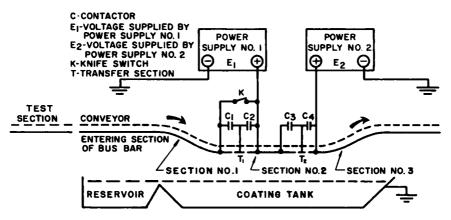


Figure 5. Typical electrical layout for step-up voltage process in electrocoat system

#### Literature Cited

Reuss, Memorabilia Soc. Imp. Nat. Moscow (1809) 2, 327.
 Hagan, J. W., Ortung, F. W., Chow, S. W., "Electrodeposition of Organic Coating," Paint Varnish Prod. (1967) 57 (4) 48-55.
 Yeates, R. L., "Electropainting," Draper, Teddington, England, 1966.
 Chandler, R. H., "Advances in Electropainting," London, 1969.
 Ranney, M. W., "Electrodeposition and Radiation Curing," Noyes Data Corp., Park Ridge, N. J., 1970.
 Stromberg, S. E., "Conductive Primers and Other EDP Advances," Ind. Finishing (Oct. 1969) 22-26.
 Gerhart, H. L., "Ultrafiltration System Recovers Coatings Lost in Electrocoating Process." Paint Varnish Prod. (1971) 61 (2) 40-41.

coating Process," Paint Varnish Prod. (1971) 61 (2), 40-41.

# Conversion and Electrodeposited Coatings: A Total Concept

JAMES I. MAURER and ROBERT M. LACY

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In the electrodeposition of paint, part of the substrate becomes an integral part of the deposited film and can influence the coating properties. This paper covers the effect on paint quality of the cleaning of the metal surface, formation of the conversion coating, post treatment, deionized water rinsing, and dryoff conditions. The system is evaluated for salt spray and humidity resistance, adhesion, filiform corrosion, detergent resistance, and uniformity of paint film. For maximum selectivity of paint, the proper conversion coating, a reactive post treatment, and the dryoff oven should be used. By carefully matching the paint formulation with the conversion coating, quality finishes can result, even if post treatment and the dryoff oven are eliminated. Electrodeposited paints require a more uniform and complete coating than conventionally deposited paints.

It is accepted practice to clean and to treat metal surfaces to produce on them a conversion coating before applying industrial paint finishes (1,2). Conversion coatings as a base for paint have been proved valuable during many years of field use, which have shown that they provide a simple, economical means of substantially increasing the overall quality of painted products.

Proper metal preparation, including the formation of a surface conversion coating prior to painting, contributes to painted product durability by:

(1) decreasing the spread of corrosion of the substrate metal at areas where the paint film is broken, and in this way materially reducing the

loss of paint that would ordinarily lift and peel away as a result of the action of the alkaline corrosion products.

- (2) preventing or decreasing on zinc surfaces the reaction of the zinc metal with the paint by virtue of the fact that the conversion coating is a non-metallic, non-reactive separating layer.
- (3) controlling the action of moisture which permeates the paint film to a substantial degree. This eliminates or minimizes blistering under high humidity conditions, thus contributing to paint film integrity.
- (4) improving the mechanical paint adhesion by increasing the surface area, and/or providing a capillary bed (3) into which the organic finish can penetrate.

Conversion coatings are produced by the chemical reaction of a coating solution with the metal surface. In most cases, components of the metal surface react with components of the coating solution to produce a tightly adherent, water-insoluble inorganic coating on the metal. The metal surface is thus rendered non-metallic.

Cleaning and conversion coating can be combined into one step. Processes of this type are generally referred to as cleaner-coaters. Much greater flexibility in operation and usually higher quality can be obtained, however, by separating the cleaning and the conversion-coating step and by post treating the conversion coating to further enhance its ability to hold paint and minimize corrosive attack of the metal surface.

A typical processing sequence before conventional paint application today would consist of:

- (1) Cleaning the metal, 60-90 seconds
- (2) Water rinse, 30 seconds
- (3) Treatment to obtain a conversion coating, 60 seconds
- (4) Water rinse, 30 seconds
- (5) Post treatment or final rinse, 30 seconds
- (6) Dryoff in oven

The two basic methods of treating metal surfaces are by the immersion process and by the spray process (4, 5). The immersion process is the older and the simpler and consists of dipping the product to be treated in tanks containing the treatment solution. Most high production treatments of preformed metal parts today, however use the chemicals by the spray process. The spray process, in this case, is not the application of the solution using finely dispersed particles, as is the case of the application of paints by spray, but rather by flooding the preformed parts by impinging the solution onto the metal surface through nozzles that have relatively high volume capacity and which are designed to produce a minimum breakup of solution. The solution draining from the parts runs back to a reservoir tank and is constantly recirculated onto the work and continually reused. Conversion coatings can be produced by brushing or wiping a treating solution on the metal surface. Portable, heated spray

equipment or steam generating equipment can be successfully used to apply conversion coatings outdoors or where spray or immersion equipment is unavailable. Normally these latter methods are used for limited production or for large or heavy items.

One large use of painted metal is the painted coil-postformed approach to the production of items such as roof decking, building siding and trim, and many other applications where the product can be formed after painting. Since the metal is flat and in coil form, it can be pulled through a stripline where each of the processing stages are separated by squeegee rolls. This process features very short treatment times and very high line speeds (6). Both immersion and spray processes are used.

#### A New Dimension

Until the introduction of electrocoating (7, 8, 9), the method of application of the paint film had little if any bearing on the quality of the finished system. With the introduction of the electrodeposited paint film, however, it is necessary to think no longer in terms of a paint applied on a substrate but rather a paint film formed on a substrate, with components of the substrate becoming an integral part of the paint film (10, 11, 12, 13, 14, 15). With electrodeposited painting it is the interplay of the total finish system that must be considered to ensure optimum balance of quality and economy. This paper deals with the role played by conversion coatings in the total finishing system.

#### Current Practice

Various conversion coating processes are used in industry today. The type used depends on the type of metal, the combination of metals processed, and the quality requirements of a given operation. The following summarizes the type of conversion coatings available:

Steel:

- (1) Iron phosphate—a mixture of iron phosphate and iron oxide; considered to be amorphous. Coating weights in the range of 15 to 90 mg/sq ft.
- (2) Zinc phosphate—grey, crystalline, essentially a mixture of zinc and iron phosphates. Coating weights in the range of 100 to 600 mg/sq ft.
- (3) Molybdate/phosphate—a mixture of iron phosphate and molybdate with iron oxides; considered to be amorphous. Coating weights in the range of 15 to 50 mg/sq ft.
- Zinc Surfaces: (Hot Dipped Galvanized and Electrogalvanized Steel)
- (1) Zinc phosphate—essentially zinc phosphate with traces of nickel; grey, crystalline. Coating weight range of 100 to 350 mg/sq ft.