JOURNAL OF APPLIED ELECTROCHEMISTRY **13** (1983) 269–275

REVIEWS OF APPLIED ELECTROCHEMISTRY 7

Electrophoretic painting

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Received 19 October 1982

Electrophoretic deposition of paint, one of the newest industrial paint application methods, resembles electroplating of metal ions in as much as the conductive surfaces to be coated are submerged in an aqueous bath, where dispersed, ionized, organic material is deposited through the action of an impressed direct current. Electrodeposition of paint is used for the coating of merchandise ranging in size from steel building trusses and automobile bodies, metal furniture, appliances and toys, to objects as small as nuts and bolts. The acceptance of this coating technology is still accelerating as more and more industries realize the inherent advantages of the process.

1. History

The migration of clay particles suspended in water in an electric cell was reported in 1808 [1]. The next milestone in the study of this phenomenon seems to be Quinke's work, published in 1861 [2], who observed that many finely divided substances migrate towards the anode (positive electrode) in water, but towards the cathode in turpentine. Picton and Linder [3] reported in 1892 that 'Magdala-red' in absolute alcohol is repelled from the positive electrode. Magdala-red is a diamine [4], and from the current point of view can be expected to show cationic properties. In 1905, Picton and Linder were probably first to observe an electrodeposition, "Ferric hydroxide is repelled from the anode in the presence of alcohol . . . the coagulum that separates on the cathode is horn-like in appearance . . . " [5].

Working in a different area, Field and Teague [6] observed the separation of diphteria toxin and antitoxin through electrophoretic migration in agar gel. Work on electrophoretic separation techniques continued and culminated in 1937 when Arne Tiselius [7] began to publish his work on the separation of proteins, for which he received the 1948 Nobel Prize.

Wheeler P. Davey received a patent for an electrophoretic coating process in 1918 [8]. He describes the 'making and applying of japan' a product composed of 'asphalt plus oleaginous material, or condensation, or oxidation thereof, containing ammonia or other alkali' and describes the anodic electrophoretic deposition at 10–200 V. In 1923 the Anode Rubber Company, Ltd. of London obtained a patent [9] naming P. Klein of Budapest, Hungary, as inventor, claiming '. . . homogeneous deposits of india-rubber are obtained by electrophoretic precipitation . . . '. Also Crosse and Blackwell, Ltd., England obtained patents in 1936, 1937 and 1943 for the coating of food can interiors with bees wax emulsions, etc. [10, 11, 12], naming W. Clayton and co-workers as inventors. All these processes were based on the application of natural resinous materials, and by 1950 no industrial coating process based on electrophoretic deposition is known to have been in operation.

A great need for an improved coating process, however, existed, as evidenced by the deplorable piles of rusted equipment. The flat, exposed surfaces of discarded cars, appliances, etc., generally retain their paint coat in good condition, while the more hidden surfaces are severely rusted. The study of new merchandise showed that these inner surfaces did not carry a complete paint coat, due to the inability to reach these surfaces by spray painting, and due to a phenomenon called 'solvent wash'. During the baking or stoving of painted items, temperature differentials are created

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between the inner surfaces of three-dimensional structures. The solvent or water in the wet paint then evaporates from the warmer surfaces and condenses on the relatively cooler surfaces, washing down the paint coat, thus creating the condition for early corrosion. A painting process was needed which allowed the baking or curing of merchandise in virtual absence of paint solvents. This can be achieved through the electrophoretic deposition of paint solids from aqueous dispersions.

In the late 1950s the technology was available for the successful electrodeposition of paint: (a) Acidic synthetic resins had begun to appear in the 1930s and were available as waterborne spray paints in a variety of acid values and molecular weights. In fact, the body of knowledge allowed the synthesis of resins for special purposes. (b) Analytical chemistry had advanced to a point where hydrolysis, oxidation, and reduction even in the vicinity of electrodes, as well as bacterial growth, etc. could be easily determined. (c) The know-how in electrical engineering allowed the safe handling of direct currents of hundreds of volts at thousands of amperes.

In the late 1950s a farsighted group at the Ford Motor Company funded a project studying electrophoretic deposition of paint and after promising initial experiments, the concept (Fig. 1) was disclosed, in confidence, to approximately 15 paint and resin manufacturers, resulting in a system of parallel R and D efforts [13].

2. The electropainting process

The system in current use can be described as the utilization of synthetic, water-dispersable, electrodepositable, filmforming macro-ions. Originally only anionic oligomers (RCOOH) of a molecular weight of approximately 10,000 were used, where the R contains a preponderance of acrylic groups, or epoxy, or alkyd groups, etc. and these determine the properties of the final cured-out film. The oligomers, RCOOH, can be dispersed in water through the action of an alkali (Table 1), preferably a low molecular weight organic amine, like diethylamine. The anionic oligomers are reconverted to their acidic form on contact with the anode. More recently, various cationic resins, usually of the R_3N type have been synthesized [14]. These resins are solubilized through the action of weak acids.

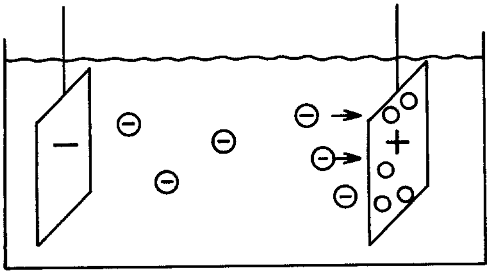


Fig. 1. Anodic electrodeposition of coatings; macro-ions are attracted to the electrode of opposite polarity.

The resulting macro-ions exhibit an electrical equivalent weight of approximately 1,600 (60 C g^{-1} or 17 mg C^{-1}). The macro-ions are applied from a bath of pH 3–7 for cationic, and pH 6–8 for anionic, at solid concentrations ranging from 6 to 20%.

Cathodic systems, in general, provide significant advances in the protection of metallic substrates [15], and exhibit 336 h corrosion resistance in saltspray tests [16]. A theory for the improved corrosion protection through cathodic materials has been developed [17], which assumes that the anodic process of metal dissolution takes place on an anodic site surrounded by a relatively cathodic and alkaline area. Thus the residual cathodic groups of paint films have a tendency to adhere to these cathodic sites. In contrast, residual anodic sites tend to lift paint films from the cathodic area which surrounds rust. Various test and field results support the above theory. The equipment for electrodeposition of paint is schematically represented in Fig. 2, and consists of:

Metal preparation. In general, a given metal preparation provides the same benefits to electrocoats as to any other paint. Zinc phosphate is recommended for highest corrosion protection. In many cases the phosphated merchandise enters the electrocoating tank wet, without phosphate dry off, as an energy saving process.

Electrocoating tanks can be classified into three groups: continuous motion; intermittent motion; and vertical entry (batch type), as schematized in Fig. 3. A counterelectrode is provided in each of these tanks, usually in one of the following two forms:

(a) The tank itself is the counter electrode. In this case, the hook which carries the mer-

Table 1

Oligomer + External Solubilizer		Solubilization $\rightleftarrows$ Deposition	Filmforming Macro-ion + Counter-ion	
R_3N	+ HX (aq)	$\rightleftarrows$	R_3NH^+	+ X^- (aq)
RCOOH	+ BOH (aq)	$\rightleftarrows$	$RCOO^-$	+ B^+ (aq)

chandise carries an insulating link, and the lower part of the hook is energized by use of bus bar and brush. In another, less widely used form, the tank is supported by insulators and all pipes are for at least part of their length, made of plastics.

(b) The tank is electrically earthed, but carries a plastic liner. All pipes are plastic or plastic lined. Counter electrodes are inserted into the tank and are sometimes surrounded by membranes. This allows at least a partial removal of counter ions.

In either case, with a grounded or insulated tank, the hooks or hangers carry a brush which contacts a bus bar, to prevent arcing.

The d.c. rectifier provides from 50–500 V, and in rare cases 1,000 V at a ripple factor not exceeding 5% over the full voltage range. Regulating transformers in combinations with silicon diodes or thyristors are used for the rectification from a.c. to d.c. The deposition voltage is selected to produce the desired film thickness from a given paint bath. The amperage ranges from 1–3 $\mathrm{A\,ft^{-2}}$ (1.2–3.6 $\mathrm{mA\,cm^{-2}}$) of surface to be painted. The amperage load starts with an initial peak which diminishes fast as the electrically resistant paint film forms. Many power sources limit not only the maximum voltage but also the maximum amperage supply, thus holding the voltage × current drawn within more uniform limits.

Immediately before, or directly over, the coating tank, electric connections with the merchandise are made, either automatically through bus bars and shoes, or manually, and are disconnected at the tank exit. A paint make-up system is provided, since the paint is delivered at concentrations ranging from 99–40% non volatiles and has to be worked into the bath. An ultrafiltrate rinse is applied onto the freshly painted merchandise as it emerges from the electrocoating tank. This rinse returns to the tank comparatively large quantities of still solubilized (ionized) paint solids which have been lifted out, but does not remove the deposited paint which is in its insoluble form (RCOOH or R_3N). The paint material lifted from the tank could actually be returned through a water rinse, were it not for the fact that the tank would overflow. The ultrafilter retains all the paint solids, while permeate (ultra-filtrate) is composed of water and the truly dissolved substances such as solubilizers, co-solvents, etc. A de-ionized water rinse removes ultra-filtrate droplets which contain paint solubilizer and may cause damage or spotting during the final cure or bake.

Bake temperatures for electropaints range from 220–375° F (378–464 K) for 10–30 min. Recently air drying electrocoats have appeared on the market. Some of these are force-dried at 195° F (364 K).

3. Unique requirements for electropaints

High pumping stability is essential since electropaints are diluted to the approximate viscosity

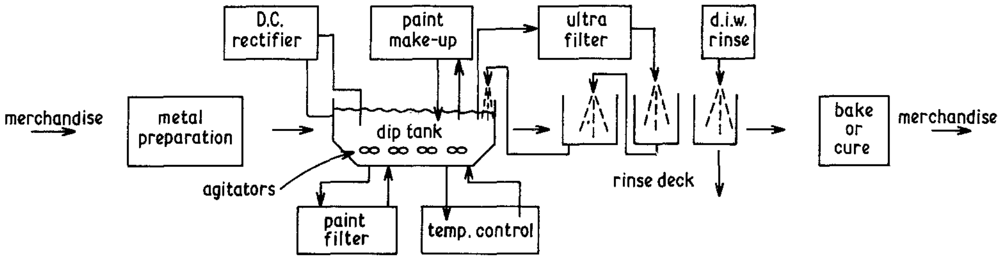
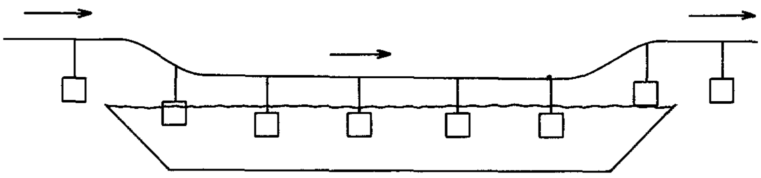
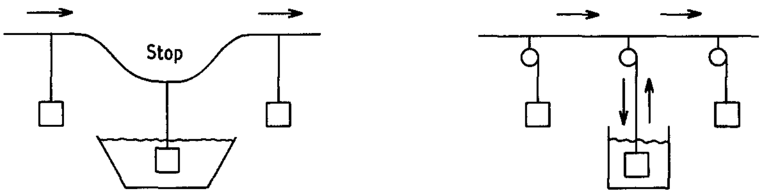


Fig. 2. Electropainting installation.



(a) Continuous motion



(b) Intermittent motion (c) Vertical entry

Fig. 3. Electropaint tanks; (a) has the largest bath volume and (c) the smallest volume per processed item.

of water and are continuously subjected to heavy agitation which creates high shear stress. A special pumping stability test has therefore been developed [18].

The solubilizer concentration has to be monitored since paint solids are coated onto the merchandise, while the solubilizer remains in the coating bath. Electropainting materials are – in first approximation – represented as RCOOH or R_3N, actually their composition is more closely represented as $R(COOH)_x$, which becomes waterdispersible through the reaction with alkali. Let us consider an oligomer with a mol. wt of 10 000, carrying ten COOH groups. If completely neutralized, a macro-ion $R(COO^-)_{10}$ would result. For electrodeposition, 10 Faradays of electricity would be needed, or we may say the electrical equivalent weight is 1000. Experience has shown that baths which contain completely neutralized oligomers have such a high solubilizer concentration that freshly deposited films are subject to resolubilization while in contact with the bath. On the other hand, if the oligomers are only neutralized by 10% to form $R \cdot (COOH)_9 \cdot (COO^-)$, it results in insufficient dispersion or low dispersion stability. The electrical equivalent weight which is most commercially desirable is 2000. Thus, we compromise and neutralize to such a degree that resolubilization and dispersion stability are within acceptable limits. Let us assume that this is the case for $(COOH)_5$–R–$(COO^-)_5 + 5B^+$, for an electrical equivalent weight of 2000. Through electrodeposition the quantity of oligomer is reduced while the counter ions remain in the bath. Thus, the degree of neutralization increases. This brings us closer to resolubilization, requires more electric current, and requires more cooling capacity, since practically all the electric energy is converted into heat. Two methods are used to keep the solubilizer concentration at a predetermined level; solubilizer re-use, that is replenishment of the bath by use of undersolubilized material, which combines with the excess solubilizer, the other method used in many installations is the solubilizer discard method, that is removal of the solubilizer rich fluid from the vicinity of the counter electrode [16].

Bath maintenance is not confined only to solubilizer control. All electrocoating bath components like pigments, co-solvents, and resin molecular weight distribution can and does change through preferential electrodeposition, filtration, hydrolysis oxidation, etc. Thus the manufacturer who develops electropaints has to study both the bath composition and the film composition. As a rule of thumb the original bath formulation is designed to give electrodeposits of the desired properties like colour, gloss, solidities, etc. The study of the film composition teaches us what materials have been removed from the bath, and therefore, have to be replaced in form of the feed.

Throwing power is the ability to deposit paint films in recessed areas, such as box sections, joints, and flanges. In fact, much of the success of electropainting is due to the excellent coverage in recessed areas. Due to the importance of throwing power, a large number of test procedures for its evalution have been developed. Ten methods of throwing power determination have been studied in one paper [19]. In the United States the Ford testing method [18] has been used widely, while more recently the General Motors method [20] seems to be preferred. The test methods for throwing power involves the design of a test piece, usually a tube or channel which acts as the electrode to be coated (or sections of which are to be coated), using either the full width of test piece for the ingress of the electric current, or slits, or holes, while the counter electrode is located outside the test piece.

Several papers deal with the theory and the parameters which allow the prediction of the depth of the deposition of electrocoats inside a cavity [21–25]. Important parameters are; voltage, bath conductivity, current requirements for deposition, conductivity of the freshly deposited film, cross-sectional area of the cell or the opening, perimeter of the opening, etc.

It is interesting to note that the distance between the electrode to be coated and a counter-electrode is not a determining parameter in the case of a comparatively small workpiece which is surrounded by a coating bath. In this case, the electric resistance between the two electrodes depends essentially on the specific resistance of the bath and the average length of the smaller electrode [26].

Throwing power as a property distinct from corrosion protection has been discussed: certain electrodeposition paints give excellent films on outer surfaces while the coat deposited on inner surfaces shows poor protecting properties [13].

4. Reasons for the worldwide acceptance of electropainting

Increased corrosion protection is one the advantages electropainting has to offer, particularly due to more uniform film thickness even in recessed areas. Large improvements in corrosion protection have been observed by the automotive and many other industries, which Hagan [27] summarized as "... electrodeposition, the most important break through ... since the invention of the spray gun ...".

Low cost when compared with other coating processes [28–31]. The cost data given in these studies cannot be compared immediately due to inflation, use of ultrafiltration, etc. However, if we assign to conventional solvent paint spray '100% cost' and compute the relative cost of other application methods in percentages, we find remarkable agreement. For installations processing approximately 45 000 ft^2 per shift, electrocoating is reported as costing 50–60% of the cost of spray painting, while the use of centrifugal electrostatic spray and powder coating is given as approximately 80% of the cost of conventional spray.

There is a virtual absence of pollution due to the use of only small quantities of volatile organic compounds (VOC) (1–2 lb. VOC per gallon of paint without water) and the very high transfer efficiencies (reported as 95–99%). Thus, the VOC emission from the prime coating or the one coat operation is reduced by 90% through the use of electropainting [32, 33]. The process is almost free from the formation of sludges.

5. Future developments required

5.1. *Paint materials free from external solubilizers*

Such materials are already available in the laboratory, based on onium bases which, like ammonium hydroxide, do not need an external solubilizer. A review paper on cathodic deposition [34], lists 6 patents on sulphonium bases ($R_3S^+OH^-$) and 2 patents on phosphonium bases ($R_4P^+OH^-$). Not only are these products ready for dispersion in water, but particularly the sulphonium bases are thermally decomposed during the bake to give products without residual ionizable groups. These paints are therefore expected to resist oxidation, saponification, etc.

5.2. *Elimination of ultrafiltrate discard*

Occasionally (and in some cases frequently) a measured volume of ultrafiltrate is discarded to free the tank from ionized impurities and from resin split products, or by-products, of low molecular weight. This practice is expensive since it discards part of the purchased paint, and requires waste treatment of large volumes, which in some cases require reduction through reverse osmosis [35].

5.3. *Prevention of membrane fouling*

A build-up of retained paint on the membrane surface in the ultra filter, also called concentration polarization, reduces the flux rate through the membrane to a fraction of attainable capacity. Promising results have been achieved in maintaining high flux rates by the use of an electric field which repels the film-forming macro-ions from the membrane [36].

5.4. *Increased corrosion protection*

Improvements in this field will always be needed. A study of the causes for excellent films on outer surfaces and poor films on inner surfaces [13] could result in great improvements.

5.5. *Air drying electrocoats*

Some are already on the market [37] and more of these products are expected.

5.6. *Low cost metal preparation*

A process using small quantities of energy is needed for electropaints and, indeed, for all other coatings.

Further information on the subject may be found in the extensive literature which has been published [38–46].

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