Production of an Adhesive Substrate Using Phosphoric Acid and a Continuous Coil Operation

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Phosphoric anodizing has been used for some time to produce very porous anodic coatings on aluminum. These coatings possess superior adhesive properties and are used in the manufacture of honeycombed panels in the aerospace industry. Recently, due to increasing governmental regulation of chromium and the costs associated with chromate conversion coatings, phosphoric anodized coatings are generating significant interest as a replacement. The paper examines the research done in the area of the adhesive properties of phosphoric anodized coatings produced on a continuous coil line. Also, the benefits of using such a surface as a replacement for chromate conversion coatings will be discussed.

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Ideal Coatings

The properties of an ideal coating have been known for some time. J. D. Edwards presented a set of criteria to describe these properties[1]. The coating should:

1. Be continuous and impervious to gases and liquids.
2. Be inert or almost insoluble in its environment.
3. Not electrolytically accelerate attack on the metal substrate.
4. Be resistant to mechanical injury and/or self-repairing.
5. Bond readily with paints and other organic finishes.

Over the years, many types of coating for aluminum have been developed to enhance the corrosion resistance and act as a primer for paints, lacquers and adhesives. They can be divided into two basic groups. Firstly, chemical oxide coatings based on various chromate and/or phosphate conversion coats and secondly, electrochemical oxide coatings produced by anodizing.

Chromate Conversion Coatings

The chemical details of conversion coats are covered in Wernick, *et al*[2], and do not need to be repeated here. Suffice it to say that for chromate type coatings, a thin outer layer of chromium ferricyanide covers a 30nm or so layer of hydrated chromium oxide which itself covers a thin boundary layer of aluminum oxide and fluoride. The various chromate coatings are in use today as a primer for both organic coatings and adhesives.

In general, it is recognized that the optimum chromate coating weight for adhesion is less than that for corrosion protection. This is recognized in ASTM B-449-67 specification as follows:

Class 1 -For maximum corrosion protection (unpainted) - 3.2 to 11 mg/dm^2.
Class 2 -For corrosion protection and paint base – 1.1 to 3.8 mg/dm^2.

For continuous application in paint lines, the trend today is to use *no rinse* or *dry in place* chromate systems to reduce the problems associated with hexavalent chromium in the waste water stream.

For the most part, chromate coatings meet the Edwards' criteria and were it not for the environmental issues around chromium and the needs of the aerospace industry, our story could end here.

Anodizing

Anodizing can be defined as the controlled electrochemical oxidation of a metal, where the oxide produced relatively inert and provides protection of the metal itself. Aluminum, titanium and to a lesser extent magnesium, have oxides that are relatively inert chemically and hard mechanically. All three metals can be anodized. We will restrict our discussion to aluminum.

In general, anodizing is carried out in a cell containing an acid electrolyte and a DC circuit whereby the work piece is the anode. The composition and morphology of the oxide film produced is a function of the chemical and electrical conditions. To day, most anodizing uses sulfuric acid as the electrolyte, but other acids can be used. For example chromic and phosphoric acid and several organic acids are used in specialized anodizing applications. There are many good texts with theoretical and practical information available on anodizing. We recommend Werwick *et al*[3] for detailed information.

The growth of the anodic film is a competition between the rate of oxidation at the metal-film interface and the rate of dissolution at the film-electrolyte interface. Eventually oxidation and dissolution reach steady state and the film achieves its maximum thickness. There are two basic types of sulfuric acid anodizing, namely "hard" and "soft".

Hard anodizing produces the most corrosion and abrasion resistant coating possible on aluminum. It is widely used for the protection of aluminum parts in aerospace structures. In sulfuric acid, the conditions for batch hard anodizing are shown in Table 1. This process is clearly expensive, with anodizing times up to 4 hours required. It does produce the thickest and most dense films protective film.

For less rigorous applications, anodizing can take place in a bath with elevated temperature and acid concentration. The conditions for soft anodizing are also shown in Table 1. This process produces a durable hard film suitable for most applications including exterior architecture. Because of the higher acid concentration and temperature, the film in this case has a porous morphology. These pores can be used to adsorb dyes for coloring. For maximum corrosion resistance, the pores must be closed by sealing, a process of hydration of the oxide in boiling water.

Hot sulfuric acid anodizing can be left to run to steady state producing an interesting film morphology. Manhart and Mozelewzki[4] showed that the pores in anodic films are tapered and as a consequence, evolve through the structures shown in Figure 1. As dissolution continues, the pores overlap resulting in the spire type structure illustrated.

Phosphoric Acid Anodizing

Anodic structures such as the spires in Figure 1 are of great interest to engineers wishing to use adhesives to bond aluminum pieces. Unfortunately, using the conditions normally associated with sulfuric acid batch anodizing, it can take several hours to achieve. To speed the process, different anodizing conditions and an acid with faster aluminum oxide dissolution rates is required. To this end, phosphoric acid is a good choice and Marceau *et al*[5] developed a patented process for The Boeing Company whose conditions are summarized in Table 1.

Continuous Coil Anodizing

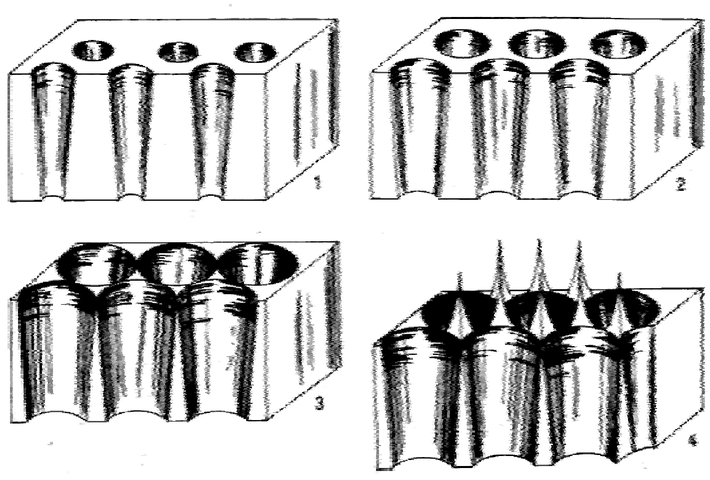
The conditions available in continuous coil anodizing are considerably different when compared to batch anodizing. The biggest advantage being the ability to introduce large electric currents to the sheet with out overloading the point contacts associated with racking in the batch process. This allows current densities an order of magnitude greater than the batch process, giving film growth rates that are measures in seconds, not minutes or hours.

Given this advantage, researchers at Lorin embarked on a program to develop a process to economically produce continuously anodized, high adhesive surface products. Using the knowledge taught by the Marceau *et al* patent, we developed the processes to produce the anodic films discussed in the balance of this paper.

Table 1.Batch Anodizing Conditions for Various Processes

Process	Hard	Soft	Boeing
Acid	H_2SO_4	H_2SO_4	H_3PO_4
Conc. %	7	15-20	10
Current Amp/dm^2	2-5 DC	1-2 DC	DC
Voltage	23-120	14-22	10-12
Temp°C	-5 to +5	18 to 25	23 to 25
Time min.	To 240	10-60	20-30
Film mm	To 250	3-35	1-2

Figure 1.

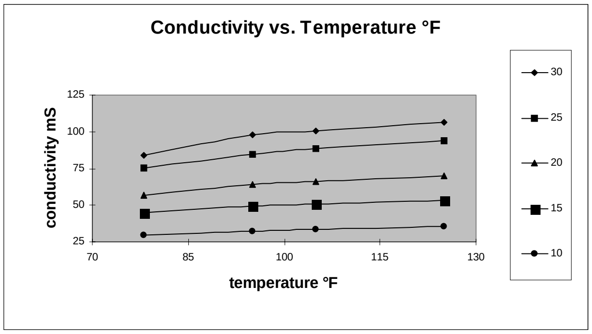


DRAWINGS OF SURFACE OF OXIDE SHOWING PORES AT FOUR STAGES OF DEVELOPMENT DURING ANODIZING OR DISSOLUTION

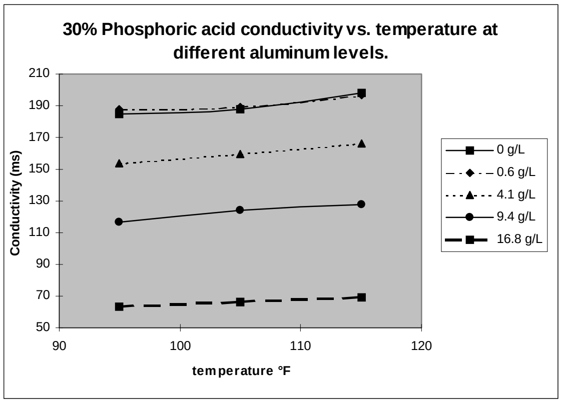
Scale-Up

Because pore structure is a competition between film growth and film dissolution, anodizing conditions need to be controlled in order to produce the proper film properties. These conditions were evaluated in the laboratory to act as pilot for the continuous coil line. In order to achieve maximum line speeds, conductivity data was gathered for solutions of various phosphoric acid concentrations, aluminum contents, and bath temperatures. Graphs 1 and 2.

Graph 1: Conductivity of Various Strength Phosphoric acid Solutions vs. Temperature.



Graph 2: 30% Phosphoric Acid Conductivity vs. Temperature at Different Aluminum Concentrations



As the concentration of phosphoric acid is increased, the conductivity increases proportionally. In addition, the bath temperature will also increase conductivity. These two factors will allow for an increase in current density to be applied to the sheet. In order to accommodate this increased current and it's effect on film growth, the increase in temperature will also need to provide increased dissolution so that the desired pore properties may be obtained. Finally, aluminum concentration will also need to be controlled in the bath. As can be seen in Graph 2, there is a marked decrease in the conductivity at all temperatures as the aluminum concentration increases. According to these results, current density could decrease by as much as 15% for a 2g/L increase in aluminum. Such a decrease in line speed on a continuous coil line would be unacceptable.

Although increasing conductivity is good for increased line speeds, the resulting film dissolution must be able to compete with this increased film growth. Figures 2,3,4, and table 2 show that as the concentration is increased, the increased acid concentration will continue to dissolve the coating, but that film thickness will continue to increase until leveling out when using 25-30% acid.

Figure 2: PAA, 15% Phosphoric Acid

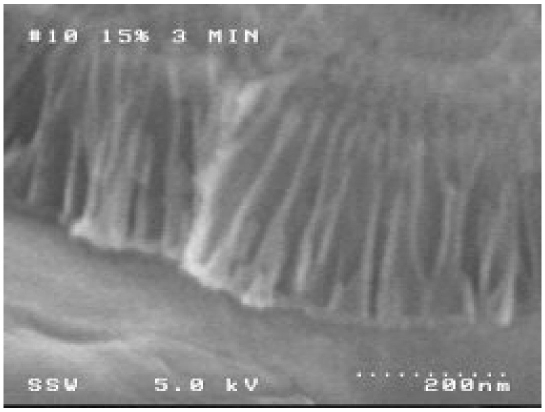


Figure 3: PAA, 30% Phosphoric Acid

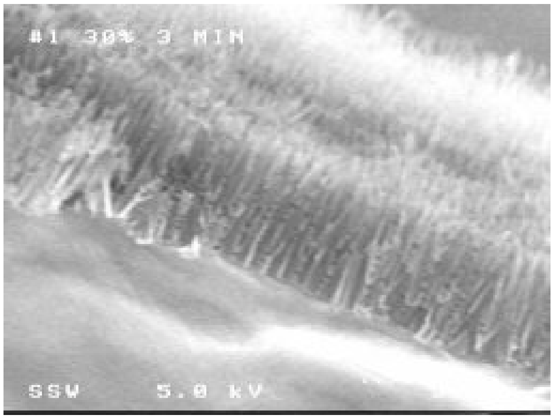


Figure 4: PAA, 20% Phosphoric Acid

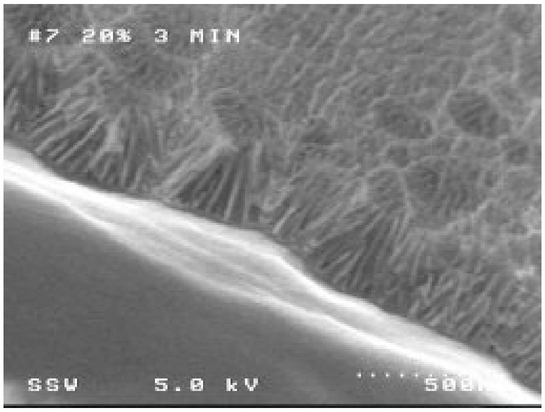


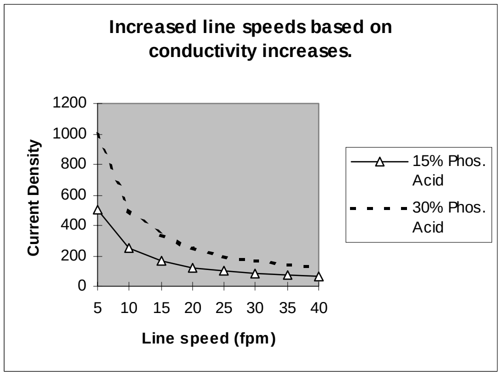
Table 2: Anodic Oxide Measurements (nm) at Various Acid Concentrations

Sample	*Barrier Layer*	*Pore Size*	*Pore Diameter*
30%	15	380-450	10-40
25%	15	400-450	20-40
20%	15	250-300	20-40
15%	15	250-260	20-30
10%	15	190-200	20-30

There does appear to be a thickening of the cell wall. This is due to increased current density and decreased dissolution of the cell walls due to the lower solubility of aluminum at higher phosphoric acid concentrations.

Knowing the current density to produce given pore geometries, predictions can be made in regards to line speed in a continuous coil operation. In this case, because phosphoric anodizing has been run on a continuous coil line previously, scale up could be based on the current densities of those previous runs, and using the data above. Graph 3 shows the predicted increase in conductivity and subsequent prediction for increased line speed.

Graph 3: Predicted Line Speeds at Estimated Current Densities.



Experimental

Aluminum was phosphoric anodized at temperature ranges of 32-50º Celsius. Constant current densities from 22.8 to 0.9 amp.s.m^{-2} were available. Concentration of phosphoric acid in the bath ranged from 0-10g/L. The time in the bath ranged from 6 minutes to 30 seconds. Alloys used were 5152 and 3003. The groups given in table 3 below were used for measurements of pore properties and adhesion testing.

Table 3: Conditions Analyzed for On-Line Test

Group	*Anodize Temp.*	*Acid Conc.*	*Time*
1	T_1	$[H_3PO_4]$	S_1
2	T_1 + 11ºC	$2[H_3PO_4]$	$S_1/3$
3	T_1 + 11ºC	$2[H_3PO_4]$	$S_1/6$
4	T_1 + 11ºC	$2[H_3PO_4]$	$S_1/8$

Results

Pore properties are listed in table 4 for each group. As expected, film thickness increases with greater current density. By increasing the conductivity of the solution as was done for group 2 from group 1, we are able to increase the speed of the line by 100-200%. The classic spire structure is still present and the pore diameters are very close, if not indistinguishable from one another. It should be noted that the pore diameters given below are from a sample of different alloys. When compared against the same alloy, group 2 actually appeared to show slightly larger pores, although more data is needed to show statistical significance.

Table 4: Pore Properties of Groups 1,2,3,4. (All measurements in nanometers.)

Group	***Barrier Layer***	***Oxide Thickness***	***Pore Diameter***	***Cell Thickness***
1	23-28	820-890	30-60	15
2	25-30	870-950	20-110	15
3	25-30	270-300	20-100	45
4	22-30	180-290	20-100	45

Upon increasing the speed, the cell wall thickness increases. This of course is reasonable given the decreased dissolution time. A resulting loss in the spired shaped pores confirms that film dissolution is now being over taken by film growth. This resultant increase in cell thickness can have important implications for future designs of an optimal line for producing these types of materials.

Also noticeable in side views of the anodic film (Figures 5 and 6) are distinct phases where the film appears to be layered.

Figure 5. PAA Showing Two Layered Film Profile

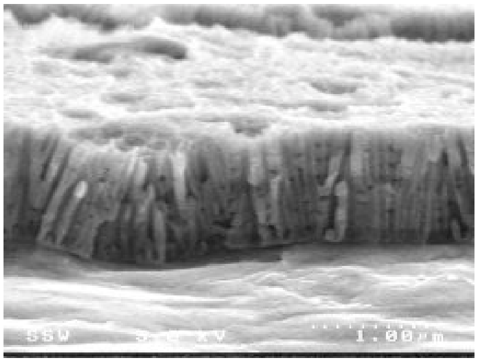
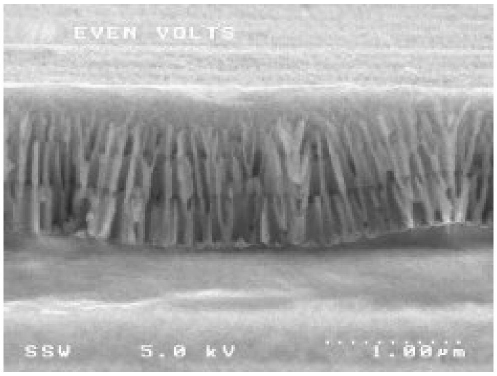


Figure 6: PAA, Film Profile with Three Layer Structure.



This layering occurs when the material passes through each flow cell with current. The phenomenon appears in constant voltage and amperage conditions and also in conditions where the volts and amps are purposely raised from the beginning to end of anodizing. This layering is bound to occur due to the dissolution between flow cells. During this time, the cell wall dissolution proceeds. Upon reentering the anodize cell, a new resistance to voltage develops initially, and then proceeds at an even rate once the rate between film dissolution and film growth is established. Because of the larger pore size and increased rate over that of a sulfuric anodized part, this phenomenon is very evident in phosphoric anodize processes.

Adhesion

After reviewing the effect various conditions had on line speed, further experimentation was performed to evaluate the adhesion properties of these conditions. ASTM D1876-95 Standard Test Method for Peel Resistance of Adhesives (T-Peel) and ASTM D1781-93 Standard Test Method for Climbing Drum Peel for Adhesives were used to see if there were significant differences between the various pore geometries. The adhesive used for these tests was 3M's DP420 Epoxy. A commercially available chromate conversion coating was used to provide a baseline for adhesion in the T-Peel test. Data for the peel strength tests are given in table 5 and 6.

Table 5.
T-Peel Tests on Various PAA Conditioned Coils.

ASTM D 1876	**Chrom. Conv.**	**G1**	**G2**	**G3**	**G4**
Avg. kg.cm^{-1}	2.0	1.6	*3.8**	2.4	1.7
Std. Dev. kg.cm^{-1}	0.5	0.1	*0.8*	0.3	0.6

Table 6.
Drum Peel Tests on Various PAA Conditioned Coils

ASTMD 1781	G1	G2	G4	G3
Avg. (cm-kg/cm.)	12.3	*22.9**	4.9	3.9
Std. Dev. (in-lbs./in.)	2.4	*3.9*	1.2	0.5

**Cohesive Failure Occurred*

In all cases, the phosphoric anodized pieces far outperformed the chromate conversion coatings. Even the pieces with thinner film thickness and larger cell walls showed adhesion levels four times better than the chromate conversion coatings. There is a significant increase in adhesion levels for those samples produced to group 2 conditions. Although group 1 and group 2 appear to share similar pore properties, there is a definitive difference in adhesion values. Additional data collection is needed, but it is hypothesized that group 2 properties may be more open to accept the adhesive, while group 1 still has macro-cell structures which may not be allowing full surface contact throughout the surface. The effect of viscosity and pore size still needs to be considered and remains to be reported upon.

Corrosion Testing

While phosphoric anodized samples have always shown good adhesion compared to chromate conversion coatings, their corrosion resistance has often been questioned. Recent testing in this study suggests that phosphoric acid anodized (PAA) samples tend to corrode more quickly around exposed areas. However, chromate conversion coatings have exhibited higher levels of blistering when compared to the PAA material. This blistering might lead to catastrophic failure of the paint system. In addition, the chromate conversion coatings appear to be more susceptible to filiform corrosion than the PAA material. Current tests are underway to evaluate the effect that increased cell wall thicknesses have on PAA material's corrosion characteristics.

Effect of Cleaners on PAA Material

Group 1 material was exposed to various acidic and alkaline cleaners at standard operating conditions for those specific cleaners. The samples were not contaminated prior to cleaning in order to test the maximum effects cleaners had on these surfaces. T-peel tests were then used to determine if there was any degradation in adhesive quality. Figure 7 and Table 7.

Figure 7: Alkaline Cleaned PAA Material.

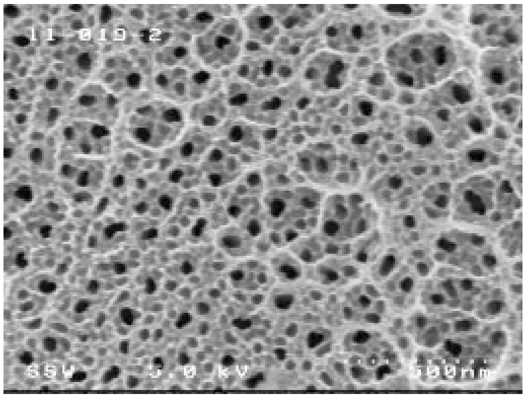


Table 7: ASTM D1876 T-Peel of Acid and Alkaline Cleaned PAA, Group 1 Material.

Cleaner Conditions	Average ($kg.cm^{-1}$)	Std. Dev. ($kg.cm^{-1}$)
Alkaline 1 min. soak	2.0	0.1
Alkaline 3 min. soak	2.0	0.1
Alkaline 5 min. soak	2.1	0.3
Acidic 2 min. soak	1.5	0.1
Acidic 6 min. soak	1.6	0.1
Acidic 10 min. soak	1.7	0.2

No degradation in adhesive strength was noted. There was a slight increase in strength for the alkaline cleaned material. This increase in strength may be due to dissolution of the cell walls just enough to allow the glue to achieve maximum surface area between the top and bottom of the pores. Further testing on this material will be gathered in the future.

Conclusion

The use of phosphoric acid anodized aluminum to produce an excellent substrate for adhesive applications has been demonstrated. In coil anodizing, the phosphoric process may be scaled up to the continuous line, once the conditions for pore formation and pore dissolution are known. The electrochemical conditions can be selected for rapid film growth and pore morphology development. The test data indicates that these coatings should be considered as a viable and superior alternative to chromate conversion coatings.

References:

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