# **Recognition and Statement of Problem**

Chromic acid has been used for decades within industry to treat metal surfaces. Two common applications involving chromic acid have been: 1) to increase the corrosion resistance of a metal surface and 2) to prepare a metal surface for adhesive bonding.

Although processes such as these have been very useful in industry and have been used for decades, chromic acid possesses hexavalent chromium, which is now known to be a carcinogen. Therefore, in recent years, there has been significant effort to find alternative processes that can be used in place of chromium-containing processes.

For non-adhesive bonding applications involving aluminum surfaces, the use of an alternative, sulfuric acid-based replacement process has been used successfully for the past decade. Although this process produces an aluminum oxide layer with corrosion resistance properties comparable to those of the chromic acid process, this oxide layer does not possess comparable adhesion properties. Therefore, the sulfuric acid-based process cannot be used in place of the chromic acid version for critical adhesive bonding applications.

Electrolytic, phosphoric acid based treatments are known to “open up” the outer surface in aluminum alloys and the open nature of the surface can improve adhesion properties. One of these phosphoric acid based processes has been used successfully as a deoxidizer pretreatment process; however, this deoxidizer process was developed as a pretreatment for a different anodize process and has generally not been used as a pretreatment for the sulfuric acid based anodize process described above. Furthermore, sulfuric acid is strongly acidic, and opening up the surface may lead to a retention of sulfuric acid. This residual acidity might interfere with the curing mechanisms of adhesive and primers, thereby reducing overall adhesion properties.

To counter the effects caused by possible residual acidity, the use of a bicarbonate, neutralizing dip after the sulfuric acid process can be employed. This surface neutralization technique has been used successfully in other industrial processes involving strong acids.

Finally, the application of certain silicon-based coupling agents has been known to improve adhesion and other properties on various inorganic materials. Certain titanium, zirconium, and aluminum-based chemicals have also been used, sometimes in conjunction with the silicon-based coupling agents.

By combining the sulfuric acid based anodize process with the deoxidizer pretreatment, the neutralizer post treatment, and the application of adhesion promoting coupling agents, preliminary adhesion studies have shown excellent adhesion properties under most test conditions. However, results of tests performed at cold temperatures (-65oF) have exhibited extreme variability; in some instances, cold temperature results were very poor.

Due to these poor results at low temperature, it was decided to perform a designed experiment on this combination process to determine if parameters could be adjusted to improve cold temperature adhesion properties.

# **Choice of factors, levels and ranges**

In creating this combination process, note that the various individual steps -- the deoxidizer pretreatment, the sulfuric acid based anodize process, the bicarbonate neutralization step, and the application of a coupling agent treatment -- were extracted from other processes. These individual procedures had not previously been used in combination with each other. Consequently, in the preliminary studies involving this combination of process factors (prior to this designed experiment), levels of the individual factors were set at the standard values normally used in the other processes. For this designed experiment, the center points were assumed to be these same standard levels, and low and high points were selected from each side of the center points.

In this experiment, parameters related to the sulfuric acid anodize were not varied since this process must meet other requirements (e.g., corrosion resistance), and variation of the parameters related to this process might affect those properties. However, factors related to the other three process steps (the deoxidizer, the neutralization, and the coupling agent application steps) were varied and are shown in TABLE I.

**TABLE I. Descriptions of Experimental Factors.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Factor Description | **Main**  **Factor**  **Designation** | **Low**  **Level**  **(-)** | **Center**  **Point** | **High**  **Level**  **(+)** |
| Time used in phosphoric acid-based pretreatment process (prior to sulfuric acid process) | A | 7 min | 10 min | 13 min |
| Voltage used in phosphoric acid-based pretreatment process (prior to sulfuric acid process) | B | 5 volts | 7.5 volts | 10 volts |
| Concentration of sodium bicarbonate neutralizing solution (used after sulfuric acid-based process) | C | 2.0% | 5.0% | 8.0% |
| Time soaking in sodium bicarbonate neutralizing solution (used after sulfuric acid-based process) | D | 5 sec | 55 sec | 105 sec |
| Amount of silicon-based coupling agent in adhesion-promoting solution | E | 5 ml | 10 ml | 15 ml |
| Amount of zirconium-based coupling agent in adhesion-promoting solution | F | 2.5 ml | 5.0 ml | 7.5 ml |
| Immersion time of panel in mixed (silicon+zirconium) coupling agent solution | G | 30 sec | 120 seconds | 210 sec |

1. **Selection of the Response Variable**

As mentioned above, we have previously obtained good adhesion results on sulfuric acid processed surfaces by using the phosphoric acid deoxidizer pretreatment and by using bicarbonate neutralizing bath and organosilane-based coupling agent treatments as post treatments. However, we have had extreme variability of our adhesion results when these surfaces were tested under cold conditions. Since acceptable adhesion properties at cold temperature have been difficult to obtain, this experiment specifically focused upon the adhesion peel strength (using a standard, ASTM D 3167 test procedure) performed under cold temperature conditions (-65oF).

1. **Choice of Experimental Design**

The experiment was performed using a 27-3 fractional factorial design (Resolution IV) in two confounded blocks, as shown in TABLE II below. Twenty total runs were performed, with each block of ten runs performed on a separate day. (A “run” is defined in the next section.) Blocks were defined by the sign of the ABD interaction term. Within each block, runs were performed in random order, except for the first and last run of each day/block, which were center point runs.

**TABLE II. Experimental Design.**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Run  ID # | A | B | C | D | E =  ABC | F =  BCD | G = ACD | *Block*  *=ABD* | *Run*  *Order*  *Day #1* | *Run*  *Order*  *Day #2* |
| 1 | - | - | - | - | - | - | - | - | 6 |  |
| 2 | + | - | - | - | + | - | + | + |  | 4 |
| 3 | - | + | - | - | + | + | - | + |  | 8 |
| 4 | + | + | - | - | - | + | + | - | 4 |  |
| 5 | - | - | + | - | + | + | + | - | 7 |  |
| 6 | + | - | + | - | - | + | - | + |  | 5 |
| 7 | - | + | + | - | - | - | + | + |  | 3 |
| 8 | + | + | + | - | + | - | - | - | 1 |  |
| 9 | - | - | - | + | - | + | + | + |  | 7 |
| 10 | + | - | - | + | + | + | - | - | 2 |  |
| 11 | - | + | - | + | + | - | + | - | 9 |  |
| 12 | + | + | - | + | - | - | - | + |  | 9 |
| 13 | - | - | + | + | + | - | - | + |  | 2 |
| 14 | + | - | + | + | - | - | + | - | 8 |  |
| 15 | - | + | + | + | - | + | - | - | 5 |  |
| 16 | + | + | + | + | + | + | + | + |  | 6 |
| 17 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |  | 1 |  |
| 18 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |  | 10 |  |
| 19 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |  |  | 1 |
| 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |  |  | 10 |

1. **Performing the Experiment**

In this experiment, a “run” consisted of the treatment of one {0.025” x 4” x 9” aluminum panel} and one {0.063” x 4” x 8” aluminum panel} processed together at the appropriate factor levels shown in the table above. These two panels were then bonded together with an adhesive and cut longitudinally into three 1”wide strips. Using a mechanical test with temperature-controlled chamber set to –65oF, each 1” wide strip was tested by positioning in a separating, roller-type apparatus, which was placed inside a cold (-65oF) test chamber and attached to mechanical test machine grips. After a 10-minute soak period at –65oF, the specimen was peeled apart in the cold chamber using a constant speed of motion, and the average force required to peel the specimen apart was determined. This average value is called the “peel strength” of the specimen, with units of {pounds per inch width}.

With twenty runs and three specimens per run, sixty individual peel strength specimens were generated and tested. Since it was not possible to test all these specimens within a single time period, testing was performed on three separate days. The three specimens obtained from each run were separated into three different test groups, and each group of twenty specimens was tested on a different day in random order.

Therefore, for each run, the average of the three test specimens (tested on separate days) was the response variable for the run.

Sufficient planning, preparation and care were used prior to and during the experiment so problems could be avoided, and fortunately, no significant problems were encountered during the experiment. The run chart used during this experiment is shown in Figure 1.



**Figure 1. Run Chart Used during Experiment.**

Experimental test results are shown in TABLE III.

**TABLE III. Experimental Results; -65oF Peel Test.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Run ID # | Test #1  (test day 1) | Test #2  (test day 2) | Test #3  (test day 3) | Average Peel  Strength (piw) | Standard Deviation (piw) |
| 1 | 7.7 | 5.4 | 9.0 | 7.37 | 1.82 |
| 2 | 25.4 | 25.1 | 30.4 | 27.0 | 2.98 |
| 3 | 25.0 | 27.3 | 26.5 | 26.3 | 1.17 |
| 4 | 18.5 | 8.6 | 11.1 | 12.7 | 5.15 |
| 5 | 24.4 | 14.4 | 24.7 | 21.2 | 5.86 |
| 6 | 26.4 | 16.3 | 24.9 | 22.5 | 5.45 |
| 7 | 27.8 | 25.9 | 32.4 | 28.7 | 3.34 |
| 8 | 19.8 | 17.9 | 21.5 | 19.7 | 1.80 |
| 9 | 23.1 | 27.4 | 37.3 | 29.3 | 7.28 |
| 10 | 11.3 | 7.0 | 14.4 | 10.9 | 3.72 |
| 11 | 19.9 | 8.2 | 18.8 | 15.6 | 6.46 |
| 12 | 25.8 | 23.9 | 26.9 | 25.5 | 1.52 |
| 13 | 25.3 | 20.9 | 26.2 | 24.1 | 2.84 |
| 14 | 17.3 | 15.5 | 15.0 | 15.9 | 1.21 |
| 15 | 20.1 | 19.6 | 23.0 | 20.9 | 1.84 |
| 16 | 37.0 | 28.6 | 40.6 | 35.4 | 6.16 |
| 17 | 9.9 | 15.0 | 9.3 | 11.4 | 3.13 |
| 18 | 10.6 | 8.8 | 13.2 | 10.9 | 2.21 |
| 19 | 29.2 | 19.9 | 19.1 | 22.7 | 5.61 |
| 20 | 21.5 | 17.2 | 18.6 | 19.1 | 2.19 |