Use of Fume Suppressants In Hard Chromium Baths—Quality Testing

By T.D. Ferguson, M. Zellen, D. Brennan & J. Lutz

The EPA Common Sense Initiative (CSI) is a cooperative effort of government, industry, environmental and other stakeholder groups to find "cleaner, cheaper, smarter" approaches to environmental management in industrial sectors. The purpose of the project is to help hard chromium metal platers reduce plating tank emissions in order to comply with, in a cost effective manner, or exceed, EPA's Chromium Emissions MACT Standard. The major objective of this project was to assess and evaluate pitting in hard chromium plating when using wetting-agent-type fume suppressants. Bench-scale testing, followed by full-scale production testing, permitted investigation of the effects of various operational parameters, such as plating time and current density, on whether pitting would occur or be aggravated in the presence of fume suppressants on various base metals. Evaluation of various pre-treatments were also tested to determine the potential for quality problems when using fume suppressants.

Background

This Phase II project is an extension of work done in 1997 under sponsorship of the Environmental Protection Agency (EPA) and the National Institute of Standards and Technology (NIST)—referred to as Phase 1 of the Hard Chromium P2 Demonstration Project. Phase 1 evaluated various control technologies to meet the EPA MACT standard as well as wetting-agent-type fume suppressants (FS). Fume suppressants were added to three plating bath tanks with associated emission control devices and the emissions were tested. Observations of these limited tests indicated dramatic results in terms of inlet and outlet emission reductions at relatively low cost.

During literature research and user surveys, it was found, however, that the hard chromium plating industry had traditionally regarded FS as unsuitable for use because of safety issues and pitting problems. Pitting has been identified as (1) defects in the base metal, along with inadequate base metal preparation (in this case, the chromium deposit attempts to bridge the base metal pit but is not always successful); and (2) hydrogen (gas) pitting that occurs within the chromium deposit. Millage and Hague[1] hypothesize that fume suppressants "aggravate" hydrogen pitting as a result of the longer hydrogen bubble growth and release cycle. Fume suppressant suppliers indicated that a resolution of most of these problems has been achieved with the introduction, in the late 1980s/early 1990s, of third generation FS. Like the second generation FS, third generation FS are perfluorinated but with higher solubility and lower foaming. Supplemental compounds [salts] in the second generation FS, when mixed with the fluoride ions in the plating bath, became suspended and caused roughness, porosity and cracking on the chromium plate during hard chromium plating operations. This additive is not present in the third generation FS, so problems associated with pitting have been reduced. This led to an initiative by EPA to conduct a follow-on focused study of FS effectiveness in meeting the MACT standard for hard chromium plating.

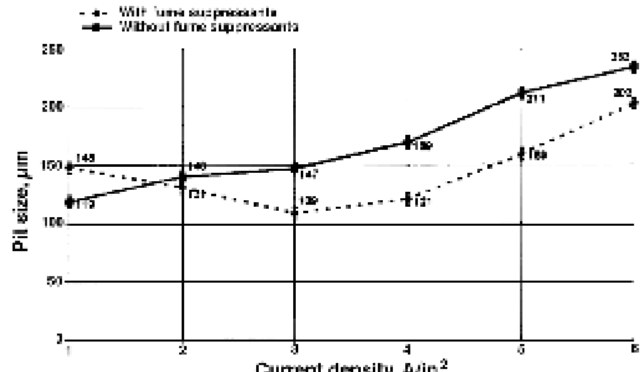

Fig. 1—Hull Cell test: 90 min.

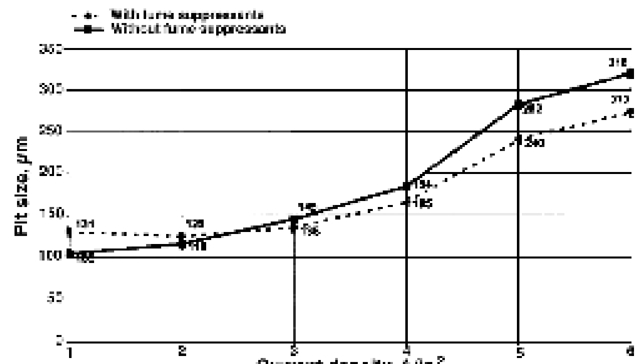

Fig. 2—Hull Cell test: 180 min.

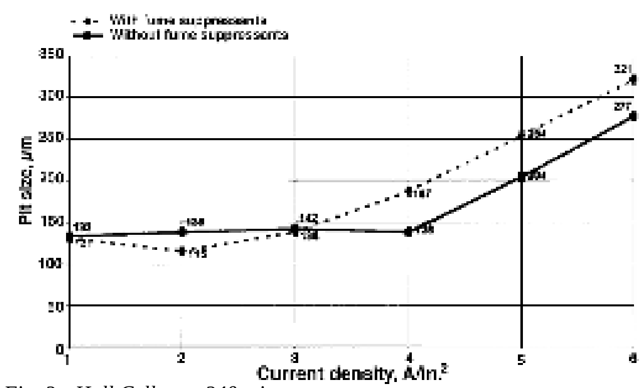

Fig. 3—Hull Cell test: 240 min.

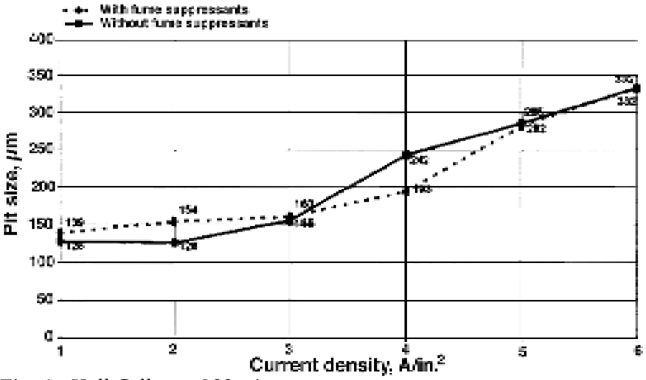

Fig. 4—Hull Cell test: 300 min.

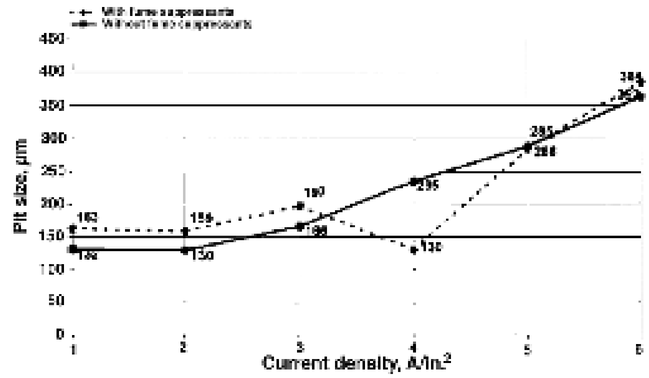

Fig. 5—Hull Cell test: 360 min.

Test Protocol

In the December 2, 1997 Expert Advisory Panel (EAP) meeting, a matrix format was recommended to identify the relevant research variables for potential investigation, and to begin the design of experiments. The matrix was developed by the EAP; industry representatives indicated that production-scale testing of the variables thought to impact plated part quality would be necessary. Based on these discussions, the following hypotheses were developed to guide the design of the quality testing protocol.

Table 1
Pretreatment Test Results

Pretreatment	Current density, asi	Time, min	Pit size* µ	Coating thickness, in.
Reverse etch (2 A/in.^{2} for 5 min)	2	120	140	0.0013
Reverse etch (3 A/in.^{2} for 5 min)	2	120	125	0.0011
Reverse etch (4 A/in.^{2} for 5 min)	2	120	145	0.0012
Reverse etch (2 A/in.^{2} for 10 min)	2	120	130	0.0012
Reverse etch (3 A/in.^{2} for 10 min)	2	120	140	0.0013
Reverse etch (4 A/in.^{2} for 10 min)	2	120	140	0.0013
Abrasive blast	3	120	150	0.0015
Bead blast	3	120	185	0.0013
Heat treat	3	120	170	0.0015
Abrasive blast	4	120	240	0.0020
Bead blast	4	120	200	0.0020
Heat treat	4	120	200	0.0021
Abrasive blast	2	300	210	0.0023
Bead blast	2	300	175	0.0019
Heat treat	2	300	200	0.0023
Abrasive blast	3	300	245	0.0044
Bead blast	3	300	260	0.0043
Electroclean	3	300	275	0.0048
Heat treat	3	300	240	0.0040
Acid etch	3	300	235	0.0036
Abrasive blast	4	300	245	0.0051
Bead blast	4	300	275	0.0049
Silica blast	4	300	245	0.0052
Electroclean	4	300	300	0.0059
Heat treat	4	300	305	0.0054
Acid etch	4	300	285	0.0044

* Reported pit size is the average pit size measured to the nearest 5 µm.

1. Pre-treatment Methods
   —If the parts are not "properly cleaned," pitting will occur.
   —Aluminum oxide blasting will aggravate pitting.
   —Glass bead blasting will not aggravate pitting.
2. Substrates
   —High nickel alloy tool steels have been reported as more likely to pit.
   —Welded and reworked parts are reported to pit more frequently.
   —Using fume suppressants in hard chrome plating of cast iron will aggravate pitting.
3. Thickness of the Plating
   —It has been reported[2] that pitting is not aggravated by FS use in chromium plating thickness up to 800 µm (32 mil).
4. Bath Contaminants
   —The presence of bath impurities increases the likelihood of pitting.
   —Particles floating on the surface of the bath may contribute to pitting.
   —Foaming caused by fume suppressants may contain impurities that contaminate the plated part.
5. Current Density
   —High current densities increase the likelihood of pitting.
6. Type of Fume Suppressant (Chemistry)
   —Some fume suppressants have longer "staying power" than others. Recent products are more chemically stable.
   —Foaming characteristics of fume suppressants impact quality, and worker perception of emission control.

Based on these hypotheses, the quality testing was divided into Hull Cell testing, confirmatory testing, pre-treatment testing and alloy testing. The results of these tests are described below.

Hull Cell Test/Confirmatory Test

A modified Hull Cell was used during the Hull Cell test. A Hull Cell is an apparatus that allows optimization of current density range, optimization of additive concentration, recognition of impurity effects and indications of macro-throwing-power capability. The Hull Cell was modified by suspending it in the tank. The Hull Cell was designed for direct immersion in the plating tank and to allow for re-circulation of the bath across the face of the panel. The panels used are the same

Table 2
Additional Pretreatment Test Results

Pretreatment	Current density, asi	Time, min	Pit size* μ	Coating thickness, in.
Salvage	2	2880	>480	0.0358
Salvage	2	2880	>480	0.0342
Ground	3	300	225	0.0053
Welded	3	300	240	0.0033
Reworked	3	300	210	0.0024
Ground	4	300	280	0.0060
Welded	4	300	260	0.0049
Reworked	4	300	255	0.0040
Cast Bar	4	120	No pits	0.0040
Cast Bar	4	120	No pits	0.0039
Cast Bar	4	120	No pits	0.0041
Cast Bar	4	120	No pits	0.0038

* Reported pit size is the average pit size measured to the nearest 5 μm.

Table 3
Combination Pretreatment Test Results

Pretreatment	Current density, asi	Time, min	Pit size* μ	Coating thickness, in.
Heat treat/electroclean	3	300	165	0.0048
Heat treat/silica blast	3	300	215	0.0046
Heat treat/bead blast	3	300	235	0.0047
Heat treat/electroclean	4	300	325	0.0056
Heat treat/silica blast	4	300	260	0.0063
Heat treat/bead blast	4	300	245	0.0053
Watts pre-plate	4	300	290	0.0079

* Reported pit size is the average pit size measured to the nearest 5 μm.

size as the panels needed for a 1000-mL Hull Cell. High-nickel alloy (A-286) panels (0.042 in. thick) were used during the Hull Cell test. The panels were drilled with a line of holes perpendicular to the lead or high current density edge of the panel. The holes (with an initial diameter of 130 μm) were drilled to represent pits. Panels made of 4130 alloy were used as the control. All panels were cleaned with an acetone rinse and reverse etched for 20 sec. The high-nickel panels were reverse etched for only 20 sec because of concern for smutting on the panel surface. Panels were later reversed for as much as 10 min to test for panel overetching. Short etch times are very common for problem alloys.

The panels were mounted on the Hull Cell and suspended in a hard chromium electroplating tank with FS. The plating bath was operated at 130 °F (±2 °F) with a chromium concentration of 30 to 34 oz/gal at a chromium/sulfate ratio of 100:1. The electroplating tank was set at 30 A and the Hull Cell tests were run at different time intervals (90, 120, 180, 240, 300, 360 and 420 min). The Hull Cell allowed the current density to be varied from 1 to 6 A. The surface tension was measured with a tensiometer in accordance with ASTM D-1331-89 and was found to be approximately 30 dynes/cm.

The results of the Hull Cell tests indicated that new pits were not formed on the high-nickel panels. The panels with the drill holes were measured with a microscope in accordance with ASTM B733 and there appeared to be pitting aggravation as the current density and the time interval increased. To determine whether the pitting aggravation was caused

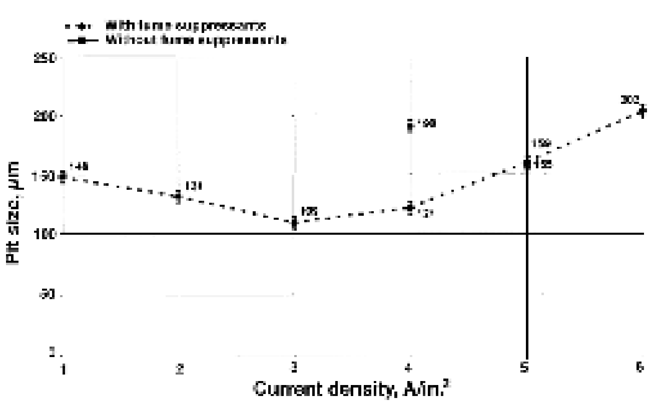

Fig. 6—Confirmatory test: 90 min.

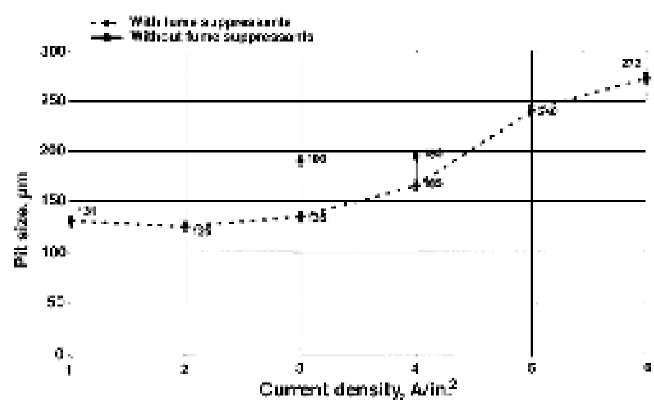

Fig. 8—Confirmatory test: 180 min.

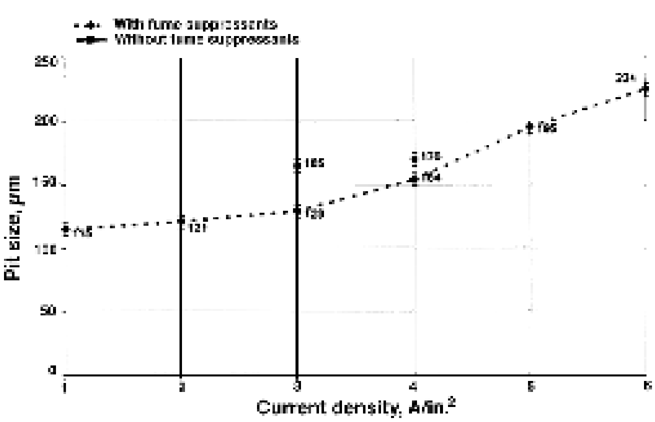

Fig. 7—Confirmatory test: 120 min.

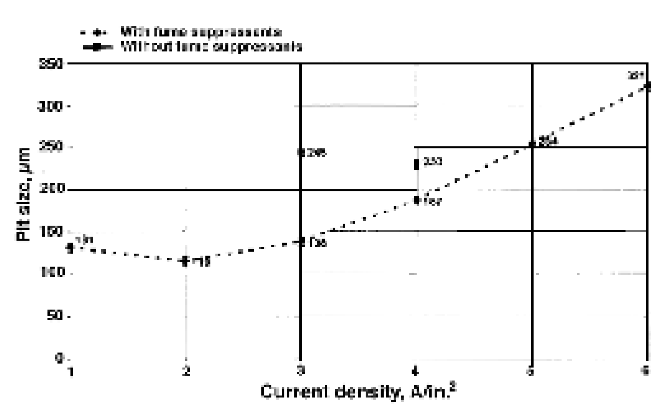

Fig. 9—Confirmatory test: 240 min.

Table 4
Alloy Test Results

Alloy	Current density, asi	Time, min	Pit size* µ	Coating thickness, in.
15-5	3	300	245	0.0030
17-4	3	300	240	0.0040
410	3	300	225	0.0027
1010	3	300	210	0.0026
4130	3	300	185	0.0034
347 (with FS)	3	300	230	0.0036
347 (w/o FS)	3	300	230	0.0041
15-5	4	300	245	0.0038
17-4	4	300	295	0.0054
410	4	300	280	0.0036
1010	4	300	175	0.0034
4130	4	300	210	0.0044
6061 Al	4	300	No pits	0.0030
7075 Al	4	300	No pits	0.0018
347 (with FS)**	4	300	230	0.0041
347 (w/o FS)**	4	300	230	0.0049

* Reported pit size is the average pit size to the nearest 5 µm.
** 347 alloy had new pit formation of highly variable size and shape.

Table 5
Alloy Test Results

Alloy	Current density, asi	Time, min	Pit size* µ	Coating thickness, in.
15-5	3	300	210	0.0030
410	3	300	205	0.0041
347	4	300	250	0.0048
15-5	4	300	245	0.0040
17-4	4	300	205	0.0051
410	4	300	290	0.0047
1010	4	300	285	0.0060

* Reported pit size is the average pit size to the nearest 5 µm.

by FS or by the increased current density and time interval, the Hull Cell tests were re-run in an electroplating tank without FS. The same results were found—no pitting formation, only pitting aggravation as the current density and time intervals increased. Figures 1-5 show the results of the current density on pit size as a function of time, with and without FS.

The confirmatory tests were performed following the Hull Cell tests. The purpose of the confirmatory tests was to show that the Hull Cell tests represented normal operating conditions. The high-nickel alloy panels, both drilled and undrilled, plus the control panels, were placed in the electroplating bath and tested at 90, 120, 180, 240, 300, and 360 min. The two current densities (before and after the change in the slope of the current density vs. pit size) chosen for each time interval were based on the results of the Hull Cell tests. For example, the current densities tested for the 90-min time interval were 4 and 5 A/in.^{2}, and for the 180-min time interval were 3 and 4 A/in.^{2}. The confirmatory test results show that there is a relatively good correlation between the pit size with and without the Hull Cell. The results of the confirmatory tests are included in Figs. 6 through 11.

Confirmatory testing was completed at two other locations. The confirmatory testing at the first location was operated for 300 min at current densities of 3 and 4 A/in.^{2}. The confirmatory testing at the second location was operated for 300 min at a current density of 4 A/in.^{2}. The results of the testing at these two additional locations also showed that there is a relatively good correlation between the pit size with and without the Hull Cell.

Pretreatment Evaluation

Various pre-treatment methods were tested to determine whether these methods affected the quality of the substrate. The drilled and undrilled high-nickel alloys with the 4130 alloy control were treated prior to plating. Many different pre-treatment technologies have been evaluated: aluminum oxide abrasive blast (100 grit), glass bead blast (100-170 grit), silica blast (90-170 grit), electroclean (50 sec anodic then 10 sec cathodic at 2 A/in.^{2} for three cycles), heat treat (375 °F for 24 hr), acid etch (20-25% sulfuric acid for 60 sec), and reverse etch. The temperature of the electroclean bath was controlled at 150 to 180 °F. The pre-treated panels were then placed in the electroplating bath with FS for 120 min at 3 and 4 A/in.^{2} and/or 300 min at 2, 3, and/or 4 A/in.^{2}.

After plating, the panels were inspected and the pre-drilled holes were measured with a microscope in accordance with ASTM B733. No new pits were formed on the panels for any of the tested pre-treatment methods. The pit size did increase as the current density and time intervals increased. Table 1 shows the results of the pre-treatment tests.

Tests were conducted on other modified panels/bars in the electroplating bath with FS. These tests include ground panels, welded panels (TIG) with bead blast, reworked panels, cast bars and salvage plating (target thickness >32 mil). Analysis of these panels, as measured with a microscope in accordance with ASTM B733, indicated that no new pits were formed. The results of these tests are included in Table 2.

Combination Pre-Treatment Evaluation

The results of the pre-treatment evaluation showed that these pre-treatment methods did not cause pitting, only increased pit sizes as current density and time intervals increased, as shown in Tables 1 and 2. Additional testing was completed in an electroplating bath with FS at the given current densities and time intervals with combination pre-treatment methods. The following combinations were tested: heat treat [375 °F for 24 hr with electro-clean (50 sec anodic, then 10 sec cathodic at 2 A/in.^{2} for three cycles)], heat treat with silica blast, heat treat with bead blast, and Watts nickel pre-plate. Similar to all of the other testing, no new pits were formed. The pit sizes were measured with a microscope in accordance with ASTM B733. The results are included in Table 3.

Alloy Test

Common alloys involved in the electroplating industry were tested to determine whether quality issues were based on the type of alloy. Numerous alloys were evaluated: 15-5 (4.67% nickel, 14.19% chromium & 0.04% carbon), 17-4 (4.25% nickel, 15.35% chromium & 0.04% carbon), 410 (0.161% nickel, 12.317% chromium & 0.15% carbon), 1010 (trace nickel, trace chromium & 0.5% carbon), 4130 (0.006% nickel, 0.945% chromium & 0.31% carbon), 6061 and 7075 aluminum, and 347 (37% nickel, 26% chromium & 0.5% carbon). Half the alloy panels were drilled, except for the

6061 aluminum and 7075 aluminum that could not be drilled. All of the panels were treated with acetone followed by a 20-sec reverse etch prior to plating. The panels were plated for 300 min at 3 and 4 A/in.^{2}, except for the 6061 and 7075 aluminum alloys that were only plated at 3 A/in.^{2}.

After plating, the panels were inspected and the pre-drilled holes were measured with a microscope in accordance with ASTM B733. New pits were formed on the 347 alloy panels. The 347 alloy test was re-run in an electroplating bath without fume suppressants. New pits also formed during this test. Based on this information, pits were not caused by the FS. For the other alloys, the pit size did increase as the current density and time intervals increased. Table 4 shows the results of the alloy tests.

Table 6
Bath Constituents (Units, ppm)

Contaminant	Range
Chrome +6	113,500 - 193,000
Chrome +3	100 - 12,510
Copper	383 - 3,470
Nickel	10 - 249
Potassium	500 - 1,000
Sodium	325 - 866
Iron	3,290 - 3,950
Zinc	25 - 270
Chloride*	<100 - 15,000
Fluoride	34.8 - 84.5
Sulfates	25.8 - 54.9
Solids	10 - 520

*Results are inconclusive. One laboratory shows levels <100 ppm and another from 6400 to 15,000 ppm. Based on the quality of the plating, the lower number is most likely correct.

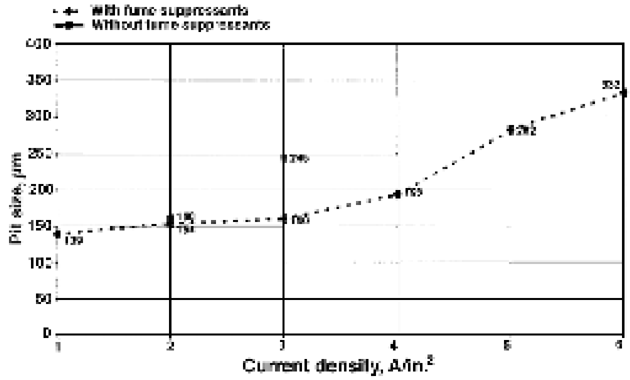

Fig. 10—Confirmatory test: 300 min.

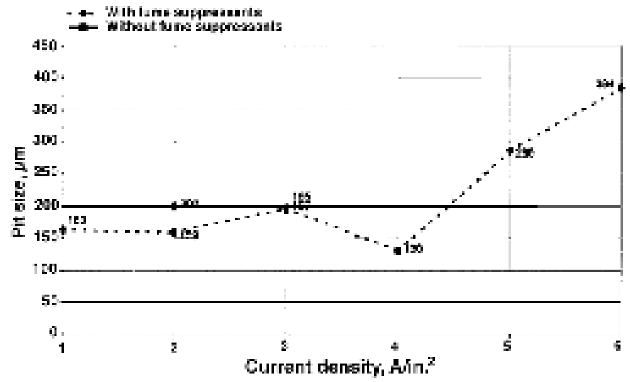

Fig. 11—Confirmatory test: 360 min.

Pre-Treatment with Different Alloys

The final testing that was completed to determine whether or not FS caused pitting was to test a pre-treatment method on different alloys. Various alloys, pre-treated with a silica blast were placed in an electroplating bath with FS at the given current density and time interval. Silica blast was tested on the following alloys: 347, 15-5, 17-4, 410 and 1010. Again, the results were the same—no new pitting was observed. Pit sizes were measured with a microscope in accordance with ASTM B733. The measured results are shown in Table 5.

Material Testing

Other testing was performed to determine whether FS affected the base material. These tests included tensile strength (hydrogen embrittlement test), microhardness and coating adhesion.

Four tensile pull bars, plated with and without FS, were tested for tensile strength in each of three classes (Class 1, Class 2, and Class 3). All of the pull bars passed the tensile strength test with scores of 90 percent or greater.

Alloy 4130 panels, plated with and without FS were measured for microhardness. The microhardness measurements for Class 1, Class 2 and Class 3 without fume suppressants were 894, 858, and 866 HV_{100} average, respectively. Similarly, with fume suppressants, the measurements were 956, 971 and 964 HV_{100} average, respectively. The average microhardness with fume suppressants was approximately 10 percent higher than without fume suppressants.

Coating adhesion was tested on an A-286 panel with a coating thickness of 0.0033 in. and on a 4130 panel with a coating thickness of 0.0034 in. Both of these panels passed the coating adhesion test (ASTM B571-91). The activation treatment was a 20-sec reverse etch at 3 A/in.^{2}. The Tensile Strength test is as in ASTM F1624. The microhardness test is as in ASTM B578-87.

Bath Constituents

Bath samples were taken for each step of testing. The purpose was to determine whether contamination of the bath caused pitting. Because no new pits were formed, contaminants were not an issue. Table 6 is a listing of the contaminants and the range over which they occurred in the various baths. This gives a good baseline to compare other tanks that may have pitting problems in the presence of FS.

Conclusions

The following conclusions can be drawn from the activities performed on this project regarding the quality of hard chrome plating in the presence of FS:

- The Hull Cell provides a relatively good representation of normal operating conditions in an electroplating bath.
- New pits are not formed on high-nickel alloys (A-286) in an electroplating bath with or without FS at current densities up to 6 A/in.^{2} and at time intervals up to 360 min.
- Existing pits are aggravated on high-nickel alloys (A-286) in an electroplating bath, with or without FS, as current density increases and time interval increases.
- Tested pre-treatment technologies (aluminum oxide abrasive blast, glass bead blast, silica blast, electro-clean, heat treat, acid etch and reverse etch) do not cause pitting formation in the presence of FS.
- Various pre-treatment methods do not change pitting aggravation significantly.
- Pits are not formed on salvaged, ground, welded, reworked panels or cast bars in the presence of FS.

- Combination pre-treatment technologies (heat treatment with electro-cleaning, heat treatment with silica blast, heat treatment with bead blast, and Watts nickel pre-plate) do not cause pitting formation on A-286 panels in the presence of FS.
- High chromium alloys (347) form new pits with or without FS in an electroplating bath. Other tested alloys (15-5, 17-4, 410, 1010, 6061 aluminum and 7075 aluminum) show no pitting in the presence of FS.
- Plating in baths with FS does not affect coating adhesion.
- Plating in baths with FS does not affect tensile strength as shown by the hydrogen embrittlement test.
- Plating in baths with FS tends to increase microhardness.

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Notice

The U.S. Environmental Protection Agency, through its Office of Research and Development, funded, managed and collaborated in the research described herein. This report has not been subject to the Agency's peer and administrative review and has not been approved for publication as an EPA document. Mention of companies, trade names or commercial products does not constitute endorsement or recommendation for use.

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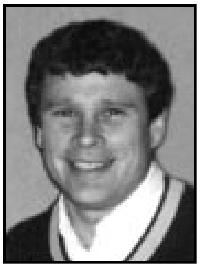

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