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NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

February 1, 1969 through June 30, 1969

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THE ADHERENCE OF PORCELAIN ENAMEL TO ALUMINUM

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U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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Progress Report

February 1, 1969 through June 30, 1969

THE ADHERENCE OF PORCELAIN ENAMEL TO ALUMINUM

by

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Sponsored by
Ferro Corp.

Porcelain Enamel Institute Research Associatship
National Bureau of Standards

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U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

I. Introduction

Since August of 1966, The Porcelain Enameled Aluminum Council of the Porcelain Enamel Institute has been studying adherence mechanisms and spalling characteristics of the porcelain enamel-aluminum system. The study has been centered at the National Bureau of Standards as a Research Associate Program, with additional technical support being carried out by member firms of the Porcelain Enameled Aluminum Council.

The failure, by flaking of the porcelain enamel away from the aluminum (known as spalling), is a major problem of the porcelain enameled aluminum industry. This failure normally occurs after weathering exposure, and its prevention on a fairly wide range of aluminum alloys plus the ability to predict its occurrence by testing prior to use are the main goals of the Program. Spalling is felt to be closely interrelated with adherence, and determining the mechanisms of adherence of porcelain enamel to aluminum has been another major part of the program.

This report has two purposes. The first purpose, covered in the Summary and the Procedures and Discussion sections which follow below, is to present the work and findings of the five month period from February 1, 1969 through June 30, 1969. The second purpose is to enumerate all the tests performed during the three year period of the program. No attempt will be made to discuss these tests in detail as to procedures or results. These tests will be listed primarily for use as a reference to past work. NBS reports numbered 9533, 9901 and 10012 cover the results of these tests in detail and can be used for detailed reference.

II. Summary

Additional information was obtained on the solution of oxide layers on aluminum by porcelain enamel. Super purity aluminum alloy 1199, which had been anodized and then chromated, showed a reduction in oxide layer thickness of 5,000-6,000 Angstroms after enameling. This agreed well with previously obtained figures for amount of solution of anodized layers. However, there is a possibility that chromium was not actually present on the oxide layer after the chromating bath, so a definite conclusion on chromium's effect on oxide layer solution rate is still open to question. It was also found that the anodized oxide layer, without any additional pre-treatment, was reduced approximately 6000Å in thickness by the porcelain enamel when the porcelain enamel contained a relatively high amount (19%) of Al_2O_3 . This is the same approximate reduction in thickness of the oxide layer as was measured using a porcelain enamel that did not contain Al_2O_3 . It would appear that the composition and nature of the oxide layer, as well as firing temperature

and time, are more important in oxide layer solution than the amount of aluminum oxide already in the porcelain enamel. The oxide layer thickness normally found on aluminum before enameling (including the thicker layers formed by prefiring) is easily within the range of thickness that the porcelain enamel can take into solution. This assumes that the layer is essentially Al_2O_3 ; the presence of magnesium in the layer complicates the situation and changes the ultimate result.

New findings with the electron microprobe and the ion probe have indicated that magnesium can be present at the interface without spalling occurring. This was found to be true with samples of 6061 which, after various extended firing times, did not exhibit spalling. The type of magnesium compound at the interface must, then, be quite important.

Various methods of exposure to high humidity and heat conditions were tried in an effort to reproduce a spall failure noted previously on prefired and enameled 5086. Although some slight spalling occurred, the gross spalling encountered before was not duplicated.

III. Procedures and Discussion

A. Electron Microprobe Analysis

Previously, samples of 1100 (prefired), 6061 (both prefired and pickled), and 5086 (both prefired and pickled) had been enameled with a firing time of ten hours. These had been cross-sectioned at 90° and submitted for electron microprobe analysis. An exploratory look indicated that this could be a fruitful area of endeavour. Accordingly, samples of 6061 (pickled) and 5086 (both prefired and pickled conditions) were enameled, with firing times of 10 minutes, 30 minutes, 1-1/2 hours and 5 hours, and prepared for electron microprobe analysis. These samples all were enameled with the standard test enamel, modified so as to contain no Cr, Fe or Al. Reynolds Metals Company and Kaiser Aluminum and Chemical, Inc. performed the microprobe analyses. The specimens from which the microprobe samples had been cut, were checked for spall resistance using 1% $SbCl_3$ spall test solution for 20 hours at room temperature. All the 5086 specimens (both prefired and enameled, and pickled and enameled) spalled badly, with an indication of slightly less spalling on the two 10-minute specimens. All the 6061 specimens exhibited excellent spall resistance.

The results of the microprobe analysis were somewhat variable. Magnesium was found at the interface in some, but not all of the samples. Reynolds detected magnesium at the interface of both the pickled 5086 and the pickled 6061 after the 5-hour fire. They also indicated heavy buildups of Mg at the interface of both the pickled and the prefired samples of 5086 fired for 10 hours. Kaiser reported magnesium at the interface on the 6061 with an apparent increase with longer

firing times. They also reported somewhat sporadic Mg buildup on the 5086 samples. The results were the most variable on the pre-fired and enameled 5086 samples. They also indicated increasing magnesium enrichments with increased firing times. This seems to be in general agreement with the Reynolds findings in that the pickled 6061 and the pickled 5086 5-hour fires and the 10-hour fire pickled and prefire 5086 were the samples showing magnesium interfacial enrichments in the Reynolds analysis.

Kaiser reported that chromium at the interface on the pickled samples decreases and virtually disappears with the extended firing times. This would appear to indicate chromium diffusion into the porcelain enamel. Visual evidence of this was seen in the fired samples. The test samples were white after the 10-minute, 30-minute and 1-1/2 hour fires, but became green-yellow with increased firing times.

A possible clue to the non-spalling reaction of the 6061 samples, despite magnesium interfacial enrichments, was further noted by Kaiser. On the 6061 samples, areas of magnesium enrichment were generally co-incident with areas of sodium and potassium enrichment. Areas of sodium and potassium interfacial enrichment on the 5086 samples occurred only in areas where magnesium was not present, or to state it another way, when magnesium enrichments were found at the interface on the 5086 samples, sodium and potassium enrichments were not present. Apparently, the form in which magnesium occurs at the interface is as important to spalling characteristics as is its presence.

During this report period, initial work was done with the ion probe. This was carried out by Kaiser on polished, unetched, 5° taper sections of pre-fired and enameled 1100 and pre-fired and enameled 5086. This work indicated no interfacial buildups on 1100 but did indicate sporadic interfacial enrichments of Mg, K, Li and O on 5086.

B. Oxide Layer Solution

Further work was carried out on oxide layer solution. Anodized super purity 1199, furnished by the Aluminum Company of America, was used for this work. In the first study, the anodic coating thickness was measured by cross-sectioning at 90° and examining the sections with the electron microscope. Several pieces were sandwiched with aluminum foil and mounted in diallylphthalate at an angle of 90°. The mounts were then rough ground, polished and lightly etched, and examined by the replica method of electron microscopy. The anodized layer was measured and had an average thickness of 28,000 Angstrom units. Pieces of this anodized 1199 were then subjected to a standard alkali-chromate pretreatment bath. These samples were then examined in the same manner as above. The chromating

bath not only altered the apparent structure of the layer, but it also reduced it in thickness from the original 28,000° Angstroms to an average measured thickness of 9,000 Angstroms. After the Chromating procedure, some sections of the chromated material were enameled with the standard test enamel generally used throughout the program. A third set of measurements was made on enameled specimens. The oxide layer thickness after enameling was reduced to an average thickness of 3,000 Angstroms. This reduction in thickness agrees quite closely with previous measurements of anodic layer solution on 1199. We have no definite proof, however, that any chromium was actually present on the anodized layer after the chromating procedure. It is possible that the action of the chromate bath was primarily one of oxide stripping with very little actual chromate deposition. Therefore, it is impossible to conclusively say that chromium has no effect on the solution rate.

A second study was carried out involving Al_2O_3 in the porcelain enamel. The standard test enamel was altered³ by removing all the TiO_2 (19%) and making a straight substitution of 19% alumina. This special enamel was then used to coat the 1199 with the anodic layer of 28,000 Angstroms. After enameling, the anodic layer was re-measured (as described above) and found to have been reduced in thickness to 22,000 Angstroms. Again, we see solution of approximately 6,000 Angstroms of anodic aluminum oxide by the porcelain enamel if the anodic coating is essentially pure Al_2O_3 as it would be here using 1199. In this range of Al_2O_3 content² of the porcelain enamel at least, the porcelain enamel still has the capability of dissolving any essentially pure layer of aluminum oxide on aluminum which has been pretreated for enameling by normal pickling or pre-fire methods.

C. Anodized Taper Sections

A second attempt was made to examine polished and anodized taper sections with the electron microscope. The first attempt had been with taper sections having the enamel on the top. Replicating these for electron microscopy fractured the thin wedge of porcelain enamel too easily. Therefore, this second attempt was made on samples with the enamel on the underside of the metal. Taper sections of this nature were made of prefired and enameled 1100 and prefired and enameled 5086.

After mounting at a 5° taper in epoxy, the samples were rough ground and polished as described previously. The polished sections were then anodized by the Aluminum Company of America. The anodizing was done in 16% H_2SO_4 at 70°F for 10 minutes with a constant 15 volts. The anodized sections were then examined for differences. Both samples could be observed to have an anodic layer; this appeared

grayish and semi-opaque under relatively low magnification. At optical microscope magnifications (in this case up to 500X), with and without polarized light, a difference was noted between the samples. The 1100 sample showed the same structure and color in the anodic coating in all areas. On the 5086 sample, however, not only did the anodic coating appear to be heavier, but as one neared the interface, the structure of the anodic coating appeared to change from what might be described as a "grainy" texture to one containing parallel lines. When the appearance of the structure changed, the color did also, changing from a light grayish-brown (under polarized light) to a dark gray.

Electron microscope replicas were also made from the same surfaces. Examination of these also showed a difference. The structure of the anodic coating on the 1100 sample did not show any change at any point on the sample as one scanned toward the interface. On the 5086 sample, however, the structure seemed to change rather abruptly as the interface between the porcelain enamel and the metal was neared. The result was an apparent band of differing structure between the enamel and the aluminum. This, however, was not identifiable as to composition.

D. Humidity Spall

Preheated and enameled panels of 5086 were examined under varying humidity and temperature conditions in an attempt to produce spalling. Previously, a sample of the same material had spalled after prolonged exposure to 100% relative humidity at 100°F followed by a short exposure to 275°F at low humidity. An effort was made to duplicate this type of spalling in a shorter period of time by employing the following cycles:

1. 100% relative humidity for 48 hours at 100° fahrenheit followed by exposure in an oven at 275°F for 24 hours.
2. Immersion in distilled water at room temperature for 48 hours followed by exposure in an oven at 275°F for 24 hours.
3. Total immersion in hot (170°F) water for 24 hours followed by 12 hours dry at 275° in an oven.
4. Suspension for 24 hours (with accompanying condensation) of the samples over an enclosed water bath with the water temperature at 170°F. This was followed by a 12-hour drying cycle at 275°F in an electric oven.
5. A "Cleveland" paint tester set with cycles of one hour condensation and one hour dry.

Method #1 yielded slight spalling after 3 complete humidity plus drying (heating) cycles. After 6 complete cycles, no additional spalling had occurred.

Method #2 showed a very small amount of spalling after the third immersion-dry cycle and additional slight spalling occurred during the 6th cycle. However, the spalling was not severe enough to constitute a failure as defined by ASTM C 486-67 or PEI Bulletin T-51.

Method #3 spalled during the hot water exposure part of the first cycle. Some additional spalling occurred during the 2nd cycle, but this additional spalling was much less. A further cycle did not yield any more spalling. This method gave the most spalling of all the five methods tried, but it was not as gross as had occurred on the long term humidity exposure failure which prompted this work.

Methods #4 and #5 did not produce any spalling. Number 4 was run for 4 cycles and #5 has been run continuously for seven weeks with no failures yet noted.

IV. Areas Studied to Date

During the first three years of this research project, the following areas have been studied and the following tests made.

A. Metals and Test Enamels

1. Metals used: 1100, 6061, 6063, 5154, 5086, 5257, 5657, 1199, 5053, 3003.

2. AL-2 was used throughout the project and, with two exceptions, the mill addition was the same. The two exceptions were: (a) in one case a removal of all color oxides and the substitution of TiO_2 for it, and (b) in the other case the removal of all TiO_2 and the substitution of Al_2O_3 for it.

B. Composition of the Oxide Layer

Alloys 1100, 5657, 6061, 6063 and 5154 were examined, with and without a 10-minute $1000^\circ F$ prefire, for thickness and composition of the natural and thermally formed oxide layers.

C. Solution of the Oxide Layer

1. Anodized 1199 and 5053 alloys were examined before and after enameling to determine the degree of oxide layer solution into the porcelain enamel. The standard test enamel was used.

2. Anodized 1199 was examined before and after enameling to determine the degree of oxide layer solution into a porcelain enamel containing large amounts of Al_2O_3 . The Al_2O_3 mill addition modification of the standard test enamel was used.

3. Anodized 1199 was subjected to a standard alkaline-chromate bath and examined before and after enameling with the standard test enamel to measure the degree of oxide layer solution into the porcelain enamel.

D. Light Microscopy

1. The following variations were examined by light microscope and photographed. These represent cross sections, both 90° and tapered, with the interface area being the area that was examined.

<u>Alloy</u>	<u>Pretreatment</u>	<u>Enamel</u>
6061	Cleaned, R-100	Standard
6061	Prefire only	"
6061	Cleaned, Vapor-plated Chromium	"
6061	Cleaned, R-100, Alkali-Chrome	"
5086	Prefire only	"
1100	Cleaned, R-100	"
1100	Prefire only	"
1100 Cladding on 6061	Cleaned, R-100 Alkali-Chrome	Commercially Enameled
5154	Prefire only	Standard
5154	Cleaned, R-100	"
5154	Cleaned, R-100, Prefired	"
5657	Prefire only	"

2. Slow motion photography with 8mm movie film and approximately 10X magnification was used to observe spalling on prefired 5154 in a 1% $SbCl_3$ spall test solution.

E. Electron Microscopy

1. The interface was examined by replica technique on the following polished, enameled cross-sections.

<u>Alloy</u>	<u>Pretreatment</u>	<u>Etch After Polishing</u>	<u>Section</u>
1100	Prefire only	None	5° taper
1100	" "	5% NaOH	5°, 175° tapers
1100	Pickled	5% NaOH	5° taper
clad/6061	Prefire only	1% SbCl ₃	5° "
1100	" "	5% NaOH-1% SbCl ₃	175° taper
1100	" "	4:1 Kellers-1% SbCl ₃	5° taper
1100	" "	5% NaOH-4:1 Kellers ³	175° taper
1100	" "	Anodized in NH ₄ tartrate	175° "
1100	" "	" " H ₂ SO ₄	5°, 175° tapers
1100	" "	Ion etch	5° taper
5154	" "	None	5° taper
5154	" "	5% NaOH	5°, 175° tapers
5154	" "	Kellers	5° taper
5154	" "	4:1 Kellers	5° "
5154	" "	1% SbCl ₃	5° "
5154	" "	5% NaOH-1% SbCl ₃	175° taper
5154	" "	4:1 Kellers-1% SbCl ₃	5° taper
5154	" "	5% NaOH-4:1 Kellers ³	175° taper
5154	" "	Anodized in NH ₄ tartrate	175° "
5154	" "	" " H ₂ SO ₄	175° "
5154	" "	Ion etch	5° "
5086	" "	Anodized in H ₂ SO ₄	5° taper
6061	" "	None	5° taper
6061	Pickled	"	5° "
6061	Prefire only	5% NaOH	5°, 175° taper
6061	Pickled	5% NaOH	5°, 175° "
6061	Clean, Vapor-plated Chrome	5% NaOH	5° taper
6061	Prefire only	1% SbCl ₃	5° "
6061	Pickled	1% SbCl ₃	5° "
6061	Prefire only	Kellers ³	5° "
6061	Pickled	Kellers	5° "
6061	Prefire only	4:1 Kellers	5° "
6061	Pickled	4:1 Kellers	5° "
6061	Prefire only	5% NaOH-1% SbCl ₃	175° taper
6061	Pickled	5% NaOH-1% SbCl ₃	175° "
6061	Prefire only	4:1 Kellers-1% SbCl ₃	5° taper
6061	Pickled	4:1 Kellers-1% SbCl ₃	5° "
6061	Prefire only	5% NaOH-4:1 Kellers ³	175° taper
6061	Pickled	5% NaOH-4:1 Kellers	175° "

2. The following direct surface replicas were also made and examined.

<u>Alloy</u>	<u>Examined</u>
1100	Surface after anodizing with H_2SO_4 .
5154	Surface after anodizing with H_2SO_4 .
6061	Mill finished surface before pretreating.
6061	Surface of sheet after exposure to a chemical cleaning bath and an R-100 bath.
6061	Surface of cleaned, R-100 treated sheet after enamel slip (wet, not fired) was allowed to sit for several minutes and then washed off.
6061	Surface replicas of enameled and spalled, preheated 6061.
5086	Surface replicas made of spalled area after humidity induced spalling.
5086	Back side of enamel flake spalled from 5086 by humidity

F. Scanning Electron Microscopy

The following variations were examined by scanning electron microscope:

1100 prefired
 5154 "
 6061 "
 6061 pickled

Kaiser and the University of Illinois performed the above work.

G. Electron Microprobe

1. Using samples with a standard 10-minute fire, the following variations were examined by electron microprobe:

<u>Alloy</u>	<u>Pretreatment</u>	<u>Enamel</u>	<u>Operator</u>
1100	Prefire only	Standard	NBS, Chromalloy Corp.
1100	" "	Color Oxide free Standard	Kaiser
1100	Pickled	"	Kaiser
1100	Clean, R-100	Standard	NBS

G. Electron Microprobe (Cont'd)

<u>Alloy</u>	<u>Pretreatment</u>	<u>Enamel</u>	<u>Operator</u>
5154	Prefire only	Standard	NBS, Chromalloy Corp., Alcan, Kaiser, Reynolds
5154	Clean, R-100	"	NBS
5154	Prefire, Clean, R-100, prefire	"	NBS
5086	Prefire only (humidity spall)	"	Alcoa
5086	Prefire only	Color Oxide free Standard	Kaiser
5086	Pickled	"	Kaiser
5053	Prefire only	Color Oxide free Standard	Kaiser
5053	Pickled	"	Kaiser
5657	Prefire only	Standard	NBS
6061	Clean, R-100	Standard	NBS
6061	Prefire only	"	NBS, Alcan, Kaiser, Reynolds

2. The following samples, with variations in firing time, were examined by electron microprobe. The enamel used was the color oxide free version of the standard test enamel.

<u>Alloy</u>	<u>Pretreatment</u>	<u>Firing Times</u>	<u>Operator</u>
1100	Prefire only	10 hours	Reynolds
5086	" "	10 min., 1/2 hr., 1-1/2 hrs., 5 hrs., 10 hrs.	Kaiser, Reynolds
5086	Pickled	10 min., 1/2 hr., 1-1/2 hrs., 5 hrs., 10 hrs.	" "
6061	Prefire only	10 hours	Reynolds
6061	Pickled	10 min., 1/2 hr., 1-1/2 hrs., 5 hrs., 10 hrs.	Kaiser, Reynolds

H. Ion Probe

Kaiser examined prefired and enameled 1100 alloy and prefired and enameled 5086 alloy using ion probe analysis.

I. Intermetallic Constituents

1. The effect of Mg_2Si particle size on spalling resistance was studied.

2. The effect of various pretreatment processes and porcelain enameling on secondary phase constituents was examined by Alcan.

J. Analysis of Spall Test Solutions

The following variations were spall tested and the spall test solutions were analyzed.

<u>Sample</u>	<u>Spall Test</u>	<u>Analysis Method</u>	<u>Operator</u>
Prefired 1100, Enameled	Dist. Water	Qual. Spectrographic	NBS
" 5086 "	" "	" "	"
" 6061 "	" "	" "	"
" 1100 "	5% NH_4Cl	" "	"
" 5086 "	" "	" "	"
" 6061 "	" "	" "	"
" 1100 "	1% $SbCl_3$	" "	"
" 5086 "	" "	" "	"
" 6061 "	" "	" "	"
" 1100 "	" "	Atomic Absorption Spectrometry	"
" 5086 "	" "	" "	"
" 6061 "	" "	" "	"
Prefired 1100, Enameled, Unenameled	Dist. Water	"	Kaiser
Pickled 1100, "	" "	"	"
Prefired 1100, "	5% NH_4Cl	"	"
Pickled 1100, "	" "	"	"
Prefired 1100, "	1% $SbCl_3$	"	"
Pickled 1100, "	" "	"	"
Prefired 3003, "	Dist. Water	"	"
Pickled 3003, "	" "	"	"
Prefired 3003, "	5% NH_4Cl	"	"
Pickled 3003, "	" "	"	"
Prefired 3003, "	1% $SbCl_3$	"	"
Pickled 3003, "	" "	"	"

J. Analysis of Spall Test Solutions (Cont'd)

<u>Sample</u>	<u>Spall Test</u>	<u>Analysis Method</u>	<u>Operator</u>
Prefired 6061 Enameled, Unenameled	Dist. Water	Atomic Absorption Spectrometry	Kaiser
Pickled 6061, "	" "	"	"
Prefired 6061, "	5% NH ₄ Cl	"	"
Pickled 6061, "	" ⁴	"	"
Prefired 6061, "	1% SbCl ₃	"	"
Pickled 6061, "	"	"	"
Prefired 5086, "	Dist. Water	"	"
Pickled 5086, "	" "	"	"
Prefired 5086, "	5% NH ₄ Cl	"	"
Pickled 5086, "	" ⁴	"	"
Prefired 5086, "	1% SbCl ₃	"	"
Pickled 5086, "	"	"	"

K. Weathering Attack

An examination of weathered, porcelain enameled aluminum was made by Alcan using light microscopy on cross sections.

L. Chromium Depositions

A surface chromium analysis was made on alloys 1100, 5086 and 6061 which had been fully pickled and which also had been cleaned and subjected to R-100 treatment only.

M. Vapor Deposition of Metal

The following metals were vapor deposited on 1100 and 5086 and the samples then checked for enamelability:

Magnesium	Iron
Copper	Chromium

N. Humidity Spalling

Various humidity and heating cycles have been tried in an attempt to induce spalling on prefired and enameled 5086.

V. Continuing Work

The following areas will be studied in an effort to further increase our understanding of the problem.

Additional electron microprobe work on "extended fire" samples will be carried out. Further variations in metal pretreatment on 6061 before enameling, coupled with the extended firing times, will be examined.

An attempt will be made to measure the solution (if any) of pure magnesium oxide into the porcelain enamel. Pure magnesium metal will be anodized, and the anodic layer thickness will be measured before and after enameling.

Anodized 5086 sealed with a dichromate solution, and anodized 5086 protected by vapor deposited chromium will also be examined before and after enameling to better determine the effect of chromium on solution rate of oxide layers.

Also to be studied will be additional spall test variations. One variation will be the deforming of various metal-pretreatment combinations after enameling; then subjecting them to several types of spall tests such as immersion in hot water, etc., as covered in Section III-D of this report. Also to be tried will be exposure to these conditions followed by the 1% SbCl_3 spall test. This will be done to check the thought that perhaps alternate moisture and heat exposure is effectively stopping any tendency to spall.

VI. Acknowledgments

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