Dec. 9, 1969 D. S. HUBBELL ETAL 3,482,951

FORCELAIN ENAMELED ALUMINUM ARTICLES

Filed July 19, 1967

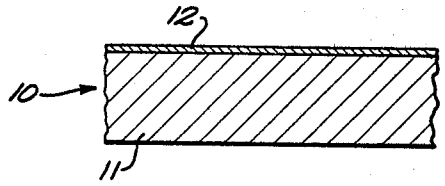


Fig. 1

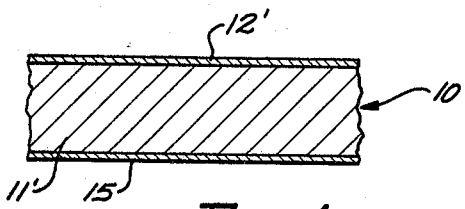


Fig. 4

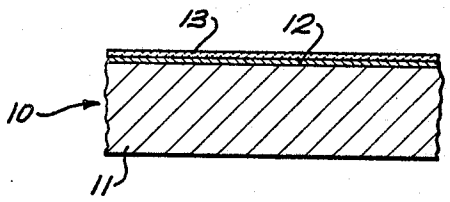


Fig. 2

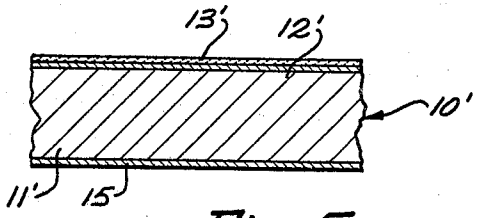


Fig. 5

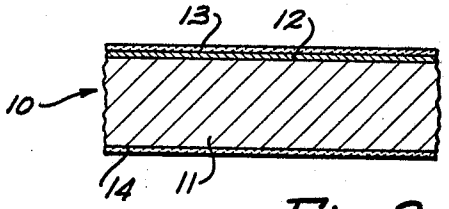


Fig. 3

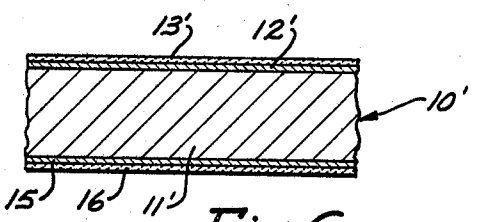


Fig. 6

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# PORCELAIN ENAMELED ALUMINUM ARTICLES

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U.S. Cl. 29—195 7 Claims

## ABSTRACT OF THE DISCLOSURE

Porcelain enameled articles are prepared from a clad aluminum sheet having a core of heat treatable aluminous alloy and having as the cladding material a high silicon-content aluminous alloy. The porcelain enameled articles can be successfully prepared without requiring the extensive precleaning and chromating which is mandatory for prior art application of porcelain enamel coatings to aluminous sheets. Spall resistance of the porcelain enamel coating is excellent.

## BACKGROUND OF THE INVENTION

### Field of invention

This invention relates to porcelain enamel coated articles having an aluminous substrate.

### Description of the prior art

Aluminum articles with porcelain enamel coatings (also called vitreous enamel coatings) have been described in various publications of the Porcelain Enamel Institute, Inc., Aluminum Division, 1145 19th Street NW., Washington, D.C. Such articles and their preparation are described in U.S. Patents 3,205,051, 3,149,001, 3,079,265, 2,932,584, 2,925,351, 2,719,796, 2,642,364, 2,608,490 and 2,544,139. Successful application of porcelain enamel coatings to aluminous substrates has required elaborate precleaning and/or pretreating. See U.S. Patents 2,719,796 and 3,149,001.

Porcelain enamel coatings have been applied experimentally to virtually every known aluminum alloy. Successful commercial products have been achieved only with a limited number of aluminum alloys, e.g., in sheet form, Alloys 1100, 3003 and 6061; in extrusions, Alloy 6061; in castings, Alloys 43, 344 and 356. (Recommended Processing Methods for Porcelain Enamel on Aluminum Alloys, Aluminum Division, Porcelain Enamel Institute, Inc., fourth edition, 1960); Alloys 3S, 52S, 51S and 43 (U.S. Patent 2,719,796); aluminum-magnesium-silicon alloys coated with pure aluminum (German Patent 1,096,149).

The porcelain enamel industry has for several years used a clad aluminum alloy sheet as a substrate for receiving a porcelain enamel coating for interior and exterior applications. Such clad sheets include a core of 6061 alloy and a cladding of lxxx alloy. Such clad alloy sheets can be enameled without darkening or discoloring, permitting application of light pastel colors in a single coat. Those clad aluminum alloy sheets, described in U.S. Patent 3,205,051 at times are prone to a defect known as spalling in which the porcelain enamel loses its bond with the substrate when exposed to the atmosphere.

U.S. Patent 3,149,001 describes a substrate for porcelain enamel coatings comprising an aluminous alloy having 0.3 to 1.0% magnesium, 1.0 to 2.2% silicon. These alloys are useful in porcelain enameling so long as a proper pretreatment with acid deoxidizer or chromate is applied.



## SUMMARY OF THE INVENTION

The present porcelain enameled articles are prepared by applying a coating of porcelain enamel slip to a clad aluminum sheet having a core of heat treatable aluminum alloys such as 6061 alloy or 7104 alloy and having a clad surface of aluminum-silicon alloy having a silicon-content from about 1.5 to 15%, but preferably from about 3 to 8% silicon. A typical useful cladding alloy is 4043. A preferred clad aluminum sheet includes a cladding of 4043 alloy on a core of 6061 alloy. The total cladding alloy thickness should constitute about 4 to 15% of the total sheet thickness.

The cladding alloy may contain other alloying metals and impurities such as copper, magnesium, iron, chromium, manganese, and zinc. The maximum content of such other alloying metals and impurities is about 2%. The magnesium content should be less than 0.1%. The copper content should be less than 0.4%. If the impurity content is as high as 2%, iron should be the principal impurity.

This clad aluminous sheet has the desirable properties:

(1) Good strength;

(2) Little or no discoloration of light colored porcelain enamel coatings;

(3) Good adhesion characteristics when pretreated by:

(a) simple degreasing or

(b) by the conventional deoxidizing treatment followed by an alkaline-chromate conversion treatment. (This treatment, described in U.S. Patent 3,149,001, produces on certain other alloys marked discoloration which requires more than one coating of light colored porcelain enamel.

The cladding for enameling purposes may be applied on one side only. Preferably the cladding is applied on both sides of the core alloy. The cladding should constitute between 4 and 15% of the sheet thickness on each side preferably about 6–8% of the total thickness. The cladding should have a minimum thickness of 0.002 inch each.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIGURES 1 through 6 inclusive are cross-sectional representations of clad-aluminum sheets and coated clad-aluminum sheets according to the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

As shown in FIGURE 1, the clad aluminum sheet **10** includes a core **11** of heat treatable aluminous alloy and a cladding **12** of a high-silicon alloy which constitutes 4 to 15% of the total sheet thickness. According to this invention, as shown in FIGURE 2, a porcelain enamel coating **13** is applied to the cladding **12** by familiar heating processes. If desired, the opposed surface, as seen in FIGURE 3, may be coated with a protective coating **14** such as paint, organic enamel, or even porcelain enamel.

Preferably, the aluminous sheet **10'** is clad on both sides, as seen in FIGURE 4. The core **11'** of heat treatable alloy is clad with the high-silicon alloy **12'** and with a further alloy **15** which is preferably the same as the high-silicon alloy **12'**. By providing both clad surfaces **12'** and **15** of the same high-silicon alloy, it is impossible to apply the porcelain enamel coating **13'**, FIGURE 5, to the wrong surface. Where the two clad surfaces **12'** and **15** are of different composition, it is possible through inattention, to apply the porcelain enamel coating **13'** to the wrong surface, i.e. to the surface **15**, and thereby fail to achieve the benefits of this invention.

As shown in FIGURE 6, the second cladding surface

15 may itself be covered with a protective coating 16 of paint, organic enamel, or even porcelain enamel.

The present clad sheeting can be successfully coated with porcelain enamel without requiring the extensive pretreatment.

The vitreous enamels which can be used are the relatively low melting point frit compositions which are readily available and which can be used at relatively low temperatures of aluminum porcelainizing—e.g. 850 to 1050° F. These enamels are normally prepared by the enameler from dry vitreous frits which are milled with water and other additives such as opacifiers, stabilizers and the like to form an aqueous slurry, called a porcelain enamel slip. The aqueous slurry is applied to the sheet by spraying in most commercial applications. Occasionally a single coat of porcelain enamel is applied to the metal sheet. In other instances, second coat of porcelain enamel is required in order to achieve satisfactory color uniformity, especially when a light-colored porcelain enamel is desired.

U.S. Patent 3,205,051 describes a clad aluminum sheet which permits application of light-colored porcelain enamel coatings in a single pass through a porcelain enameling oven. However, extensive precleaning and chromating must be carried out with the lxxx-clad aluminum sheets. The present invention can achieve single-pass porcelain enameling with medium and dark colors. However, where very light colors are required, two coats may be necessary for color uniformity.

## EXAMPLE 1

### Sheet A

Clad sheets identified as sheet A were prepared by applying a 5 percent clad coating of 4043 alloy to one side of a core of 6061 alloy by hot rolling the two alloys to a final sheet thickness of 0.080 inch.

### Sheet B

Clad sheets identified as sheet B were prepared by applying a 5 percent clad coating of 4043 alloy to one side of a core of 6061 alloy by hot rolling to a thickness of 0.125 inch. Thereafter the sheets were further cold rolled to a final thickness of 0.050 inch.

### Sheet C

A special cladding alloy I was prepared containing 5.02 percent silicon, 0.11 percent copper, 0.34 percent iron and impurities less than 0.01 percent. The alloy I was clad to one side only of a core of 6061 alloy. The cladding was 4 percent of the final sheet thickness, 0.050 inch.

### Sheet D

A clad sheet identified as sheet D was prepared by applying the alloy I to one side only of a core of 6061 alloy with the cladding constituting 10 percent of the total thickness of the sheet.

### Porcelain enamel slips

Two porcelain enamel slip formulations S–1 and S–2 were prepared as set forth in Table I.

TABLE I.—PORCELAIN ENAMEL SLIP FORMULATIONS

| Component | S–1 | S–2 |
|---|---|---|
| Frit (lead silicate type) | 100.0 | 100.0 |
| Titanium dioxide | 2.0 | 12.0 |
| Boric acid | 3.0 | 3.0 |
| Potassium hydroxide | 2.5 | 2.5 |
| Sodium silicate | 2.0 | 2.0 |
| Color oxides, black | 23.0 | |
| Color oxides, blue | | 5.0 |
| Water | 50.0 | 48.0 |

Samples of sheets A and B were degreased with an organic phosphate non-etch soak cleaner for 3 minutes at 60° C. (140° F.). A porcelain enamel slip S–1 was sprayed over the clad surface to provide a final coating thickness (after firing) of 0.003±0.001 inch. The slip was milled to a fineness of 0.2 percent retained on 325 mesh. The specific gravity of the slip when sprayed was 2.04.

The samples were fired for 10 to 15 minutes at an oven temperature between 545 and 550° C. (1010–1020° F.). The resulting coated sheets were tested by the Porcelain Enamel Institute Accelerated Spall Test in ammonium chloride. Neither sheet A nor sheet B had any evidence of spalling after the four days exposure which is the standard for determining performance in the PEI accelerated spall test.

Several samples of sheet C and sheet D were heat-treated for 15 minutes in an oven at 550° C. (1022° F.). These heat-treated samples were degreased in a 15 percent solution of sulfuric acid at 90° C. (194° F.) for one minute along with samples of sheet C and sheet D which had not been heat-treated. The degreased samples were coated with the porcelain enamel slip S–2 by spraying to a thickness of 0.003±0.001 inch (after firing).

The slip S–2 was milled to a fineness of 0.2 percent retained on 325 mesh. The slip was sprayed at specific gravity 2.04. The coated specimens were fired for 10 to 15 minutes at 545° to 550° C. (1010° to 1020° F.). The porcelain enameled aluminum samples were exposed in 5 percent ammonium chloride for 96 hours at 20° C. No spalling was observed on any of the samples of sheets C or D including those which had been heat-treated and those which had not been heat-treated.

## EXAMPLE 2

A clad aluminum sheet identified herein as sheet E was prepared using a 6061 alloy core and 1100 alloy cladding on one side only. The 1100 alloy had the following analysis:

Copper, 0.01 percent; iron 0.29 percent; silicon 0.10 percent; balance aluminum.

A clad aluminum sheet identified herein as sheet F was prepared by applying to one side only of 6061 alloy core a clad containing 5 percent silicon, 0.10 percent copper, 0.32 percent iron, balance aluminum. This cladding alloy is identified herein as alloy II. The cladding thickness for sheets E and F was 0.0024 inch average.

Six replicate samples each of sheet E and sheet F were heat-treated for 15 minutes at 550° C. (1020° F.). The heat-treated samples together with six replicate samples each of sheet E and F which had not been heat-treated were coated on the clad surface with porcelain enamel slip S-2 in the manner described in connection with sheet C and D. The coated sheets were fired for 10 to 15 minutes between 545 and 550° C. All 24 samples were immersed in 5 percent ammonium chloride solution for 26 days at 20° C. The results of this accelerated spall test are presented in the following Table II.

TABLE II

| Sheet | Preheat at 550° C., min. | Samples passing spall test after— 5 days | 10 days | 15 days | 26 days |
|---|---|---|---|---|---|
| E | 0 | 6 | 3 | 0 | 0 |
| E | 15 | 1 | 0 | 0 | 0 |
| F | 0 | 6 | (1) | 6 | 6 |
| F | 15 | 6 | (1) | 4 | 1 |

[1] Samples not tested at end of ten days.

It will be seen from inspection of Table II that the present clad aluminum sheets exhibit remarkably improved adhesion for porcelain enamel coatings when compared with the clad aluminum sheets E which are described in prior art as useful for receiving porcelain enamel coatings.

We claim:

**1.** A porcelain enameled aluminous metal article having an adherent, substantially spall-free vitreous enamel coating thereon, said aluminous metal comprising a clad sheet having a core and at least one cladding surface to which the vitreous enamel is adhered; the core being a

heat-treatable aluminous alloy and the cladding consisting essentially of aluminum having 1.5 to 15% by weight of silicon and containing less than 2% by weight of other alloying metals and impurities, of which the magnesium content is less than about 0.1% by weight and the copper content is less than about 0.4% by weight.

2. The porcelain enameled article of claim 1, wherein the core is 6061 alloy and the cladding is 4043 alloy.

3. The porcelain enameled article of claim 1, wherein the core is 7104 alloy and the cladding 4043 alloy.

4. The porcelain enameled article of claim 1, wherein the cladding is provided over one surface only of the said clad sheet and the said vitreous coating is adhered to the said cladding.

5. The porcelain enameled article of claim 4, wherein the unclad surface of the said clad sheet is covered with a protective coating.

6. The porcelain enameled article of claim 1, wherein cladding is provided on both surfaces of the said clad sheet and comprises in both claddings the same high-silicon content alloy.



7. The porcelain article of claim 1, wherein cladding is provided on both surfaces of the said clad sheet, one said cladding comprising the high-silicon alloy.

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29—197.5; 117—129