Sept. 7, 1965 D. S. HUBBELL 3,205,051

LIGHT-COLORED PORCELAIN-ENAMELED ALUMINUM ARTICLES AND CLAD-ALUMINUM SHEETS THEREFOR

Filed May 25, 1962

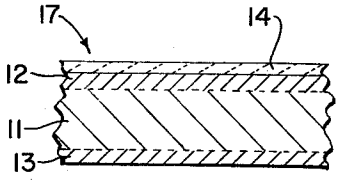



FIG. 3

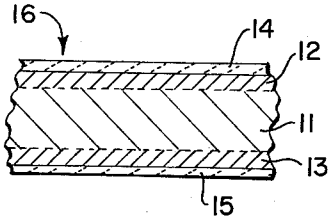



FIG. 2

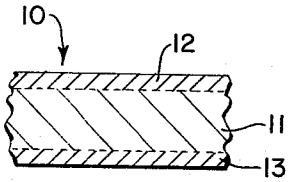



FIG. 1

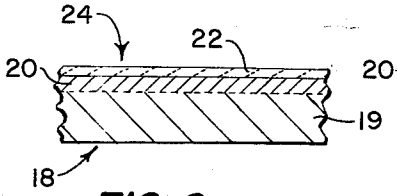



FIG. 6

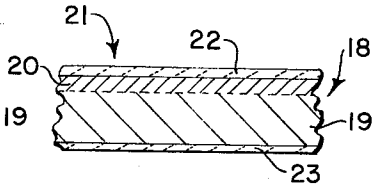



FIG. 5

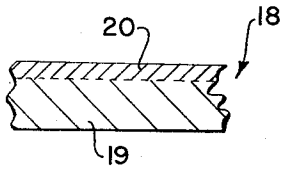



FIG. 4

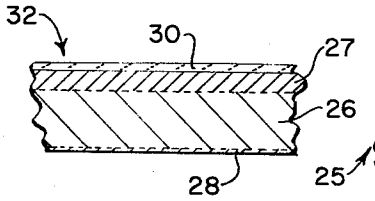



FIG. 9

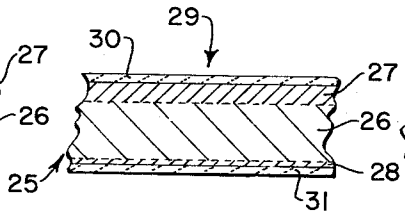



FIG. 8

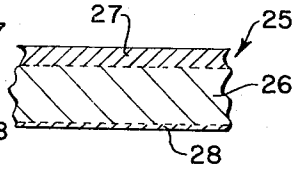



FIG. 7

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3,205,051

# LIGHT-COLORED PORCELAIN-ENAMELED ALUMINUM ARTICLES AND CLAD-ALUMINUM SHEETS THEREFOR

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6 Claims. (Cl. 29—195)

This invention relates to the art of porcelain-enameling of aluminum sheets and more particularly to improvements in the art of applying a single porcelain-enamel coating to aluminum sheets to prepare articles having uniformly light-colored porcelain-enameled coatings.

*The prior art*

The art of porcelain-enameling aluminum sheets has been described generally in U.S. Patents 2,544,139; 2,719,796; and 2,932,585. In general a porcelain-enamel "slip" is prepared as an aqueous slurry of vitreous frits for application to a clean, grease-free aluminum sheet. The aluminum sheet, coated with the "slip," is fired in an oven at temperatures of about 1000° F. to fuse the vitreous frits and allow the fused frits to form a film which adheres to the aluminum sheet. Customarily a porcelain-enamel coating is applied to both sides of the aluminum sheet to equalize stresses and thereby to avoid wrapping of the sheet which might occur if only one surface were to be coated. Occasionally, however, porcelain-enameled aluminum articles are prepared with only one surface covered with the coating since usually only one surface is exposed to view, the other surface being "hidden" from view.

The composition of the aluminum sheet which is utilized for porcelain-enameling has been the subject of considerably investigation. The presence of free magnesium in aluminum alloys introduces a tendency for spalling of the porcelain-enamel coating. Hence alloys containing free magnesium are avoided in the porcelain-enameling industry.

Similarly work-hardening alloys which become annealed on heating are avoided since the firing required to fuse the porcelain-enamel frits will cause annealing the aluminum with accompanying loss of strength and change of shape. Moreover the work-hardening alloys tend to develop hairline cracks on firing at porcelain-enameling temperatures.

The preferred aluminum alloys for porcelain-enameling are those which are heat-hardened and which contain no free magnesium. Specifically aluminum alloy 6061 is quite satisfactory. The 6061 aluminum alloy is readily available in sheets of thicknesses which are frequently desired for porcelain-enameled articles, i.e., about 0.04 to 0.25 inch thickness. The 6061 aluminum alloy moreover retains its shape throughout repeated firings where several coatings of porcelain-enamel frits are separately applied.

However, the 6061 aluminum alloy tends to discolor severely and non-uniformly when exposed to elevated temperatures in an alkaline medium. Since the porcelain-enamel frits are alkaline materials, the 6061 aluminum alloys exhibit severe and non-uniform discoloring when used in the fabrication of porcelain-enameled aluminum articles.

The discoloration of the 6061 aluminum alloy is of little consequence when relatively dark-colored porcelain-enamel coatings are provided. The relatively dark colors have sufficient opacity to mask any surface discoloration of the aluminum sheet. Hence black, dark-green, dark-blue, dark-gray and the like colors can be applied as a porcelain enamel coating for 6061 aluminum alloy articles with little difficulty. Such porcelain-enameled articles are quite satisfactory.



However, where relatively light-colored porcelain-enamel coatings are required, the discoloration of the 6061 alloy presents severe problems. The non-uniform discoloration of the aluminum sheet is visually apparent through the light-colored porcelain enamels. Heretofore the discoloration phenomenon has been compensated by providing a second coating of the porcelain enamel—requiring a second firing of the article. In more severe situations, a third coating with a third firing might be carried out to prevent the discolored aluminum sheet from adversely affecting the desired coloring of the porcelain-enamel coating.

*The present invention*

According to the present invention, a light-colored porcelain-enameled aluminum article is provided which can be prepared with a single coating in a single firing without deteriorating the light-color of the porcelain enamel. Specifically a novel, clad aluminum sheet is utilized as the base of the present porcelain-enameled aluminum article. Through the use of the novel clad aluminum sheet, the present light-colored porcelain-enameled articles of this invention are produced in a single firing.

The principal object of this invention is the production of shape retaining, light-colored porcelain-enameled aluminum articles of consistent color by a single coating and a single firing of a clad aluminum sheet.

A further object of this invention is to provide a novel porcelain-enameled aluminum article.

A still further object of this invention is to provide a novel clad aluminum sheet which is especially adapted for use in the fabrication of light-colored porcelain-enameled aluminum articles in a single coating and firing treatment.

These and other objects of the present invention will become apparent from the following detailed description by reference to the accompanying drawings in which:

FIGURES 1, 2, and 3 illustrate in cross-section the preferred embodiment of the present clad aluminum sheet; the sheet has no porcelain enamel coating (FIGURE 1); has a porcelain enamel coating over both surfaces (FIGURE 2); and has only a single porcelain enamel coating (FIGURE 3);

FIGURES 4, 5 and 6 illustrate in cross-section an alternative embodiment of the present clad aluminum sheet; the sheet has no porcelain enamel coating (FIGURE 4); has a porcelain enamel coating over both surfacts (FIGURE 5); and has only a single porcelain enamel coating (FIGURE 6); and

FIGURES 7, 8, and 9 illustrate in cross-section a further alternative embodiment of the present clad aluminum sheet; and the sheet has no porcelain enamel coating (FIGURE 7); has a porcelain enamel coating over both surfaces (FIGURE 8); and has only a single porcelain enamel coating (FIGURE 9).

Specifically the clad aluminum sheets with which the present invention is concerned are comprised of a core

of 6061 aluminum alloy with a cladding of an aluminum alloy of the 1XXX series. The cladding aluminum alloy possesses substantially the same electrochemical potential as the 6061 alloy which is the core of the sheet.

Aluminum alloys are designated by the Aluminum Association as follows:

| Aluminum Association Designation | Composition | |
|---|---|---|
| 1XXX | Silicon | 1% maximum. |
| | Iron | Trace maximum. |
| | Copper | 0.2% maximum. |
| | Manganese | 0.05% maximum. |
| | Zinc | 0.10% maximum. |
| | Aluminum | 99.0% minimum. |
| 6XXX | Silicon | 0.4-0.8%. |
| | Iron | 0.7% maximum. |
| | Copper | 0.15-0.40%. |
| | Manganese | 0.15% maximum. |
| | Magnesium | 0.8-1.2%. |
| | Chromium | 0.15-0.35%. |
| | Zinc | 0.25% maximum. |
| | Titanium | 0.15% maximum. |
| | Magnesium and silicon are the major alloying elements. The alloys are heat-hardened. | |

Heretofore the art of cladding aluminum sheets has become highly developed. In the customary cladding circumstances, a core material is selected for its structural properties and a cladding material is deliberately selected to be electrochemically sacrificial to the core. Such clad aluminum sheets are widely available in commerce. The clad aluminum sheet of this invention differs from those heretofore available in that the cladding is not sacrificial to the core, but instead has substantially the same electrochemical in order that no electrochemical sacrifice will occur.

The 1XXX series of aluminum alloys are those which are substantially pure aluminum—i.e., the impurities and alloying ingredients comprise a nearly negligible portion of the alloys.

The light-colored porcelain enamel coating of this invention is applied over the cladding surface of the aluminum sheet. The cladding surface, being comprised of an aluminum alloy of the 1XXX series, does not exhibit discoloration upon exposure to heat in the presence of the alkaline porcelain enamel "slip." Hence, the light-colored porcelain enamel coating can be applied to the cladding in a single coating in a single firing with acceptable color retention.

Aluminum sheets comprised solely of 1XXX series aluminum alloys likewise can be coated successfully with porcelain enamel coatings, but such 1XXX series aluminum alloy sheets are not utilized in porcelain-enameling since such sheets become annealed through the firing treatment and experience undesirable changes in shape during the firing of the articles. In addition, alloys of the 1XXX series tend to develop hairline cracks on the surface upon exposure to firing temperatures.

However, the clad aluminum sheets of this invention do not exhibit loss of shape during firing and do not present any hairline cracking during firing. Moreover the porcelain enamel coating which is applied to the clad aluminum sheets of this invention retains its true color since there is no detectable discoloration of the cladding alloy.

Customarily in the cladding of aluminum, a separate cladding is applied over each surface of the aluminum sheet. The provision of a cladding over each surface tends to equalize stresses which might result from the union of dissimilar alloys and thereby avoids any warping tendencies in the clad aluminum sheets. Such a "double" clad sheet, adapted to this invention, is illustrated in FIGURE 1, wherein a clad aluminum sheet **10** has a core **11** of 6061 aluminum alloy and has two claddings **12, 13** of an aluminum alloy of the 1XXX series.

The clad aluminum sheet of FIGURE 1 may be provided with separate porcelain enamel coatings **14** and **15** as shown in FIGURE 2. The porcelain enamel coatings **14, 15** may both be light colored, e.g., white, cream buff, light-grey, light blue, light-green, tan, pink, yellow, violet, orange and the like. The original coloring of the porcelain enamel frits will be retained and will be reproduced uniformly in the coatings **14, 15** without objectionable streaking.

Customarily, only one surface of a porcelain-enameled aluminum article **16** will be presented to visual observation. Hence it is a standard practice to provide some totally unrelated coloring of porcelain enamel coating on the "hidden" surface of the article **16**.

The primary purpose of providing the porcelain enamel coating over the "hidden" surface is to equalize the stresses in the article **16** and thereby to avoid any warping tendencies. The provision of the porcelain enamel coating over the "hidden" surface permits the porcelain enamel fabricator to utilize left-over batches of porcelain enamel "slips" indiscriminately since the specific coloring of the "hidden" surface is totally immaterial.

As shown in FIGURE 2, the exposed porcelain enamel coating **14** is the light-colored coating of this invention and the "hidden" surface has a porcelain enamel coating **15** of the same or an unrelated color. Note that in the article **16** of FIGURE 2, the core **11** of the aluminum sheet has a cladding **12, 13** and a porcelain enamel coating **14, 15** on each surface, thereby being completely stress equalized and free from warping tendencies. Both the coatings **14, 15** are applied concurrently and fired concurrently so that the article **16** is fabricated from a single firing.

The article **17** of FIGURE 3 utilizes the same sheet **10** of clad aluminum but provides a porcelain enamel coating **14** over only one of the claddings, to wit, the cladding **12**. Where the tendency for warping is otherwise minimized or of little significance, the article **17** of FIGURE 3 may be provided in a single firing in the light-colored porcelain enamels.

Of course, the present porcelain-enameled articles also may be provided in dark-colored enamels without loss of the desirable properties of the resulting article. However, it is only in connection with the light-colored porcelain enamels that the present articles are of especial importance.

An alternative embodiment of the invention is illustrated by the clad aluminum sheet **18** of FIGURE 4 wherein a core **19** is provided with a cladding **20** over only one surface thereof. The clad aluminum sheet **20** may be utilized to prepare a porcelain-enameled aluminum article **21** as seen in FIGURE 5 wherein the light-colored porcelain enamel coating **22** is applied over the cladding **20** and an additional porcelain-enamel coating **23** of immaterial coloring is applied over the "hidden" surface of the aluminum sheet **18** where there is no cladding.

Similarly where no porcelain enamel coating is required over the "hidden" surface of the aluminum sheet **18**, the resulting article **24** will appear as shown in FIGURE 6 wherein the light-colored porcelain enamel coating **22** is applied over the aluminum cladding **20** and the surface of the core **19** itself will serve as the "hidden" surface.

A further alternative embodiment of this invention provides separate cladding surfaces of different thicknesses as shown in FIGURE 7 wherein the clad aluminum sheet **25** has a core **26**, a relatively thick cladding **27** and a relatively thin cladding **28**.

The clad aluminum sheet **25** may be provided with a porcelain enamel coating on both surfaces as indicated by the article **29** of FIGURE 8. The light-colored porcelain-enamel coating **30** is applied over the relatively thick cladding **27** and the immaterial colored porcelain enamel coating **31** is applied over the relatively thin cladding **28**. Provision of the two claddings facilitates

fabrication of the clad aluminum sheet 25 and also serves to equalize stresses within the clad aluminum sheet 25 to diminish warping tendencies.

Alternatively the clad aluminum sheet 25 may be utilized to fabricate a porcelain-enameled aluminum article 32 as shown in FIGURE 9 wherein the clad aluminum sheet is provided with a single porcelain enamel coating 30 over the relatively thick cladding 27. The "hidden" surface of the resulting article 32 is the cladding 28.

If desired, the cladding 28 may be an aluminum alloy other than the 1XXX series, although preferably an aluminium alloy which will have the same electrochemical potential as the 6061 aluminum alloy of the core 26 to avoid sacrifice between the alloys.

It will be observed that the three illustrated clad aluminum sheets 10, 18 and 25 all possess a core of 6061 aluminum alloy and at least one cladding of 1XXX aluminum alloy.

*Examples*

*Example 1.*—A prefired sheet of cleansed, polished, 6061 aluminum alloy (0.050 inch thickness) was coated with clear (unpigmented) porcelain-enameling slip and fired at customary commercial porcelain-enameling temperatures in a commercial oven. After firing, the resulting article was inspected. The surface of the aluminum could be viewed through the fused transparent porcelain enamel coating. That surface was darkened to a deep blue, nearly black color in an uneven, streaked manner. The surface of the metal, when viewed through the transparent porcelain enamel was no longer the bright, metallic surface which was presented prior to firing.

*Example 2.*—A sheet of 1100 aluminum (thickness 0.050 inch) was coated with the clear (unpigmented) porcelain-enameling slip of Example 1 and fired concurrently with the sheet of Example 1. After firing the article was inspected. The shape of the article had changed as a result of the firing. The originally flat, horizontal surfaces had sagged severely during the firing. Nevertheless the bright metallic coloring of the sheet surface could be viewed through the transparent porcelain enamel coating. Prefiring of the sheet was not necessary.

*Example 3.*—A sheet of the clad aluminum according to this invention was obtained having a total thickness of 0.049–0.050 inch. Separate claddings of 1100 aluminum as shown in FIGURE 1 were provided in thicknesses of 6 mils each. The clad aluminum sheet was coated with the clear (unpigmented) porcelain enamel slip of Example 1 and fired concurrently with the sheet of Example 1. The shape of the resulting fired article was unchanged, i.e., there was no heat distortion manifested from the firing treatment. The metal surface, when viewed through the transparent porcelain enamel coating, was clear and bright. Prefiring of the sheet was not necessary.

Thus the comparison of Examples 1, 2 and 3 indicates that the present porcelain-enameled aluminum articles of this invention (Example 3) posses the desirable properties of the articles of the prior art without retaining their undesirable properties. Prefiring of the present clad aluminum sheets is not necessary.

The porcelain enameled article of Example 3 exhibited no spalling tendencies along its edge surface, indicating satisfactory adherence of the porcelain enamel coating.

The porcelain-enameled article of Example 3 further exhibited no evidence of electrochemical sacrifice between the cladding and the core of the clad-aluminum sheet. The lack of electrochemical sacrifice (corrosion) indicates that holes may be drilled through the present porcelain-enameled articles without creating a corrosion hazard in the region of such drilled holes.

Intensive inspection of the fired article indicated that there was substantially no migration of magnesium between the 6061 alloy core and the 1100 cladding alloy as a result of the firing exposure.



*Example 4.*—The clad aluminum sheet described in Example 3 was coated with a white-pigmented porcelain enamel slip and fired in a commercial porcelain-enamel oven. The resulting article, after the single coating and single firing, exhibited a porcelain enamel coating which retained the color properties of the original frits and further was free of non-uniformities. The clad aluminum sheet was not prefired.

*Example 5.*—The 6061 aluminum sheet of Example 1 was prefired and coated with a white pigmented porcelain enamel slip as described in Example 4. The sheet was fired in a commercial porcelain enamel oven concurrently with the sheet of Example 4. The resulting article had a porcelain enamel coating which was characterized by streaks and the lack of uniformity of the color. In some places the color appeared to be darker than the porcelain enamel frits which were applied initially. In other places the color appeared to be whiter. The whiter areas are explained by the fact that a bluish appearance of the metal surface enhanced the impression of whiteness to the viewer. The resulting article of Example 5 was covered with a further coating of the same porcelain enamel slip (white pigmented) and refired. The article resulting from the refiring had the uniform coloring which was desired, corresponding to that of the article of Example 4.

Porcelain enamel coatings on aluminum sheets normally are applied in thicknesses ranging from about 1 mil to about 10 mils, preferably from about 3 mils to about 6 mils.

Aluminum sheets for porcelain-enameling generally are provided in thicknesses of about 0.04 to about 0.25 inch. The present cladding of 1XXX aluminum alloy is provided in thicknesses ranging from about 3 mils to about 0.1 inch, with the total cladding thickness (both claddings, if two are used) being less than about 40 percent of the overall thickness of the clad aluminum sheet.

According to the provisions of the patent statutes, I have explained the principle, preferred embodiment and mode of operation of my invention and have illustrated and described what I now consider to represent its best embodiment. However, I desire to have it understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

I claim:

1. A porcelain-enameled aluminum article comprising:
an aluminum sheet having a core of 6061 aluminum alloy and an aluminum cladding alloy of the 1XXX series over at least one surface of the said core having substantially the same electrochemical potential as the said core;
a porcelain-enamel coating of fused frit film adhered to the said cladding.

2. A porcelain-enameled aluminum article comprising:
an aluminum sheet having a core of 6061 aluminum alloy and an aluminum cladding alloy of the 1XXX series over both surfaces of the said core having substantially the same electrochemical potential as the said core;
a porcelain-enamel coating of fused frit film adhered to one surface of the said aluminum sheet.

3. A porcelain-enameled aluminum article comprising:
an aluminum sheet having a core of 6061 aluminum alloy and an aluminum cladding alloy of the 1XXX series over both surfaces of the said core having substantially the same electrochemical potential as the said core;
a porcelain-enamel coating of fused frit film adhered to one surface of the said aluminum sheet and a light-colored porcelain-enamel coating of light-col-

ored fused frit film adhered to the other surface of said aluminum sheet.

4. A porcelain-enameled aluminum article comprising:
an aluminum sheet having a core of 6061 aluminum alloy and an aluminum cladding alloy of the 1XXX series over at least one surface of the said core having substantially the same electrochemical potential as the said core;
a light-colored porcelain-enamel coating of light-colored fused frit film adhered to the said cladding alloy surface and a porcelain-enamel coating of fused frit film adhered to the other, unclad surface of the said sheet.

5. A porcelain-enameled aluminum article comprising:
an aluminum sheet having a core of 6061 aluminum alloy and a cladding of 1100 aluminum alloy over at least one surface of the said core having substantially the same electrochemical potential as the said core;
a porcelain-enamel coating of fused frit film adhered to the said cladding.

6. A porcelain-enameled aluminum article comprising:
an aluminum sheet having a core of 6061 aluminum alloy and an aluminum cladding alloy of the 1XXX series over both surfaces of the said core, one such cladding having a greater thickness than the other such cladding having substantially the same electrochemical potential as the said core;
a porcelain-enamel coating of fused frit film adhered to one surface of the said aluminum sheet and a light-colored porcelain-enamel coating of light-colored fused frit film adhered to the cladding which has the said greater thickness.




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