

## UNITED STATES PATENT OFFICE

2,544,139

## PROCESS FOR ENAMELING ALUMINUM-RICH ALLOYS

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No Drawing. Application July 1, 1947,  
Serial No. 758,470

4 Claims. (Cl. 148—6.2)

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This invention relates to the enameling of aluminum-rich alloys, i. e., alloys containing at least 80% by weight of aluminum. More particularly, this invention relates to the chemical and heat treatment of aluminum-rich alloy structures followed by the application and firing of a vitreous enamel on the treated surface of the structures.

In the copending application of Alden J. Deyrup, Serial No. 635,765, filed December 18, 1945, now Patent No. 2,467,114 issued April 12, 1949, there are pointed out the difficulties entailed in the enameling of aluminum and aluminum-rich alloy structures with a vitreous enamel. The above-said copending application relates to a new enamel composition which is particularly suitable for the enameling of aluminum and aluminum-rich alloy structures.

Although these new enamels have been highly successful in the enameling of aluminum-containing structures, in the presence of water or moisture-laden atmospheres the vitreous enamels do not adhere so tenaciously to so-called "commercial aluminum-rich alloys" as to commercial aluminum, i. e., substantially pure aluminum. Commercial aluminum contains 99% plus aluminum, whereas commercial aluminum-rich alloys contain from slightly greater than 1% to 20% of particular alloying ingredients, for example, manganese, magnesium, copper, chromium, zinc and silicon. The somewhat less tenacious adherence of vitreous enamel to aluminum-rich alloys has sometimes proven to be troublesome, particularly where the enameled aluminum is exposed for long periods of time to weathering or highly moisture-laden atmospheres. This results, not always but sporadically, in a phenomenon referred to as "water-spalling," which is evidenced by a flaking-off of the enamel in tiny flakes exposing bare metal. Water-spalling starts at exposed metal-enamel interfaces, for example, at the edges of structures or at pinholes or other, normally immaterial, slight flaws in the enamel coating. Water-spalling may progress to minor failure or even to complete failure if subjected to long periods of exposure. Water-spalling may be a slow process and sometimes occurs only after weeks or months of exposure to tap water or weathering.

It is an object of this invention to provide vitreous enamel coated aluminum-rich alloys having an improved resistance to water-spalling.

It is another object of this invention to produce a vitreous enamel coated, aluminum-rich alloy which is free from water-spalling.

It is still another object of this invention to provide a process for the chemical treatment of aluminum-rich alloy structures and subsequently

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enameling the same with a vitreous enamel whereby to produce a product which is much less subject to, or free from, water-spalling.

Other objects of the invention will appear hereinafter.

The objects of this invention may be accomplished, in general, by pre-treating the surface to be enameled of an aluminum-rich alloy structure with an aqueous alkaline solution of a chromate followed by a heat-treatment at a temperature between 350° C. and the temperature at which the aluminum alloy structure is deleteriously affected by heat, usually about 600° C., and then enameling the so-treated surface with a vitreous enamel.

The aqueous alkaline chromate solution may have substantially any degree of alkalinity between pH 8.0 and pH 14. The desired degree of alkalinity may be imparted to the solution in any desired manner, for example, by the addition of alkali metal hydroxides or by the addition of salts, such as alkali metal carbonates or bicarbonates, which upon hydrolysis produce alkaline conditions.

Any chromate, including dichromates, which is soluble in water may be used for the above-said pre-treatment since it appears that the chromate ions in the solution with which the alloy is treated impart the improved adherence of the enamel to the treated surface. Alkali metal chromates are preferred. Dichromates, when added to the alkaline solution, will be converted to chromates. The chromate content may vary from 0.25% to 25%, expressed as potassium chromate, i. e., the chromate should be present in the solution in a concentration equivalent in ion content to a concentration of 0.25% to 25% potassium chromate.

The aluminum alloy structures need not generally be given a particular cleaning treatment before treatment with the chromate solution; however, if the surface of the alloy is very greasy it may be cleaned with grease solvents such as trichlorethylene, or the like.

The chromate solution may be applied to the surface of the alloy to be enameled in any desired manner; however, it is preferred to immerse the alloy structure in a bath of said chromate solution. The chromate solution may vary in temperature from room temperature (about 20° C.) up to the boiling temperature of the solution (about 100° C.). For convenience of operation, temperatures below room temperature are usually not employed. The time of treatment may vary from one to thirty minutes. After the treatment with chromate solution, it is preferred to rinse the alloy structure with water to remove any adhering chromate solution therefrom.

The above-said chromate solution treatment of



aluminum-rich alloys improves the adherence to aluminum of any vitreous enamel having a melting point below about 580° C. Best results have, however, been obtained by the use of enamels of the type disclosed in copending application Serial No. 635,765, above-mentioned. Such enamels contain:

10 to 18 mole percent PbO  
38 to 65 mole per cent SiO<sub>2</sub>  
5 to 12 mole per cent Li<sub>2</sub>O  
0 to 22 moles per cent Na<sub>2</sub>O  
0 to 20 mole per cent K<sub>2</sub>O, and  
0 to 11 mole per cent TiO<sub>2</sub>

the total alkali metal oxide content

(Li<sub>2</sub>O+Na<sub>2</sub>O+K<sub>2</sub>O)

of the enamel being between 25 and 36 mole per cent, and the ratio of the sum of said silica content and twice the said titanium oxide content of the enamel to the total alkali metal oxide content of the enamel being between 1.8 and 3.0, all of said oxides being melted into the enamel composition.

In order to obtain best results in adhesion of the enamel to the chromate-treated surfaces, the enamel should be fired at a temperature between 480° C. and 580° C., and in some cases preferably between 480° C. and 510° C. for a period of between two and thirty minutes. This applies to both ground and cover coats in case two enamel coats are applied.

It is essential that the alloy, after the chromate solution treatment and before enameling, be given a heat-treatment at a temperature between 350° C. and the heat tolerance limit of the alloy. Preferably, this heat treatment is carried out at a temperature of between 400° C. and 550° C. Such heat treatment is necessary to obtain adequate adherence of enamel to the alloy. The period of heat-treatment may vary from two to ten minutes. The heat-treatment may be carried out in an oven at atmospheric conditions.

The optimum conditions of chromate content in the alkaline chromate solution, time and temperature of treatment in the chromate solution, and firing time and temperature of the enamel will vary, dependent upon the composition of the alloy being treated. For example, in the case of the pre-enameling chromate treatment of aluminum alloy 61, containing about 0.25% copper, 0.6% silicon, 1.0% magnesium, and 0.25% chromium, with a bath containing four parts by weight sodium hydroxide, 20 parts by weight potassium chromate and the remainder water, it is preferred to treat the same for five minutes with the temperature of the bath at 50° C. In treating aluminum alloy 43, containing about 5% silicon with the same chromate bath composition, it is preferred to treat it for five minutes with the bath heated at 40° C. When treating aluminum alloy 3, containing about 1.2% manganese, with the same bath, it is preferred to treat it for fifteen minutes at a temperature of 40° C. Any of the above three aluminum alloys treated in accordance with the above-said preferred conditions may be enameled with a firing temperature of between 480° C. and 560° C.; however, in the case of aluminum alloy 52, containing about 2.5% magnesium and 0.25% chromium, it is preferred, in order to obtain optimum enamel adherence, to fire the enamel at a temperature between 480° C. and 510° C. In all of the above examples the chromate-treated alloy must be subjected to heat-treatment for two to ten minutes

at a temperature of between 350° C. and the heat tolerance limit of the alloy before enameling.

In the case of any particular aluminum alloy, it can readily be determined whether or not sufficient enamel adherence to insure against water-spalling is obtained by any prescribed course of treatment. This can be determined by means of the following accelerated test which correlates with water exposure results which may take weeks or months. This accelerated test consists in chromate-treating and enameling pieces of the particular alloy to be tested, and then exposing the enamel-metal interface by gouging, filing, or scratching the same, and immersing the test sample in 5% aqueous ammonium chloride solution for 96 hours at room temperature. If no failure occurs back one-eighth inch from the edge of the exposed interface, excellent performance in water exposure will result from the chromate treatment and enameling conditions used. The particular optimum treatment and enameling conditions for a specific alloy can thereby be established. Once optimum treatment conditions for a given alloy have been established and a chromate bath is used for continued treatment of the alloy structures or articles, it will, of course, be desirable to periodically analyze the treating bath and keep the chromate content and alkalinity of the bath within a few per cent of their initial value.

The following examples are given to illustrate certain preferred embodiments of the present invention, it being understood that the details set forth in these examples are not to be considered as limitative.

#### Example I

Aluminum alloy sheet stock composed of aluminum alloy 61 (containing, by weight, 0.25% copper, 0.6% silicon, 1.0% magnesium and 0.25% chromium) is dipped into a bath consisting of

	Parts by weight
Sodium hydroxide	4
Potassium chromate	20
Water	76

and having a temperature of 50° C. After five minutes, the sheet is removed, rinsed in tap water, dried, and heat treated at a temperature of about 500° C. for five minutes. The heat-treated sheet, after cooling, is then dipped into a water slurry of an enamel consisting of 38.1% PbO, 25.3% SiO<sub>2</sub>, 2.2% Li<sub>2</sub>O, 10.2% Na<sub>2</sub>O, 8.3% K<sub>2</sub>O, 8.7% TiO<sub>2</sub>, 2.9% Sb<sub>2</sub>O<sub>3</sub>, and 4.3% B<sub>2</sub>O<sub>3</sub>. To the water slurry is also added 3% of boric acid and 0.5% of potassium chromate, based on the weight of the water in the slurry for the purpose of obtaining better enameling. The liquid and solid contents of the slurry are mixed in such proportions that the sheet, after dipping in the slurry and draining, will contain between 15 and 30 grams (based on dry weight of enamel) per square foot for each coating; several enamel coatings, which may contain pigments or opacifying agents, with separate firings being applied if desired. The enamel is fired at a temperature between 480° C. and 515° C.

After firing and cooling, the enamel-coated structure is gouged through the enamel coating and is then placed for 96 hours in a 5% aqueous solution of ammonium chloride. The coated structure showed no perceptible water-spalling.

#### Example II

Aluminum alloy castings compound of alumi-



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num alloy 43 (containing 5% by weight of silicon) is treated with the chromate solution of Example I having a temperature of 40° C. for five minutes. The chromate-treated castings are further processed and enameled in the manner disclosed in Example I. Upon treating with an ammonium chloride solution as described in Example I no water-spalling was apparent.

Other examples of baths used to advantage to greatly reduce, or completely prevent, water-spalling contain:

	No. 1	No. 2
	Parts by weight	Parts by weight
Water.....	89.0	90.0
Potassium chromate.....	2.0	0.5
Sodium bicarbonate.....	2.0	2.5
Sodium carbonate.....	7.0	7.0

The temperature of the bath and the treatment period are adjusted for any specific alloy treated within the above-mentioned temperature ranges and treatment periods to obtain optimum results.

Successful enameling with subsequent high resistance to failure of bond under prolonged water exposure may be readily obtained by adhering generally to the following principles:

In variation of time of treatment, treatments of too short duration cause incomplete protection against water-spalling. This may be recognized by enameling test pieces and subjecting to the accelerated water-spalling test above. Treatments of too long duration result in considerable etching. This may result in a loosely adherent deposit which prevents the enamel from adhering, so that it comes off locally or generally during or shortly after cooling. It is practical to determine times of treatment, if preferred conditions are departed from, at which these two defects begin to occur, and then select a time midway between for practical use.

In variation of temperature of treatment, it is found that higher temperatures require shorter times. Speedier operation may thus be secured by appropriate temperature increase, if desired.

In variation of alkalinity, it is found that more alkaline baths cause more rapid treatment. It is desirable to avoid too rapid treatment so that time of treatment may be practically controlled at its optimal duration.

In variation of chromate content, increase of chromate content generally gives more flexibility in time duration of treatment with favorable results, but decreases the speed of action.

Aqueous alkaline chromate solutions have been used heretofore for treatment of aluminum to produce desired surface appearance and to improve corrosion resistance. Furthermore, the addition of even very large amounts of water-soluble chromates to enamel slurries and slips is without effect in preventing water-spalling. The reason why treatment with chromates and heat-treatment prior to enameling in accordance with this invention will prevent subsequent water-spalling of the enamel coating is unknown. It has, however, been definitely established that the final enameled alloy contains a chromium compound between the alloy and the enamel.

Reference in the specification and claims to parts, proportions and percentages, unless otherwise specified, refers to parts, proportions and percentages by weight.

Since it is obvious that many changes and

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modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

What is claimed is:

1. The process of producing vitreous enamel coated aluminum-rich alloys having an improved enamel bond which comprises placing the alloy surface to be enameled in contact with an aqueous alkaline solution containing between 0.25% and 25% of a water-soluble chromate for a period of between 1 and 30 minutes, heat-treating the chromate-treated alloy at a temperature between 350° C. and the heat tolerance limit of the alloy for a period of 2 to 10 minutes, and then enameling the so-treated surface with a vitreous enamel having a melting point below about 580° C. by applying said enamel to said heat-treated surface and firing the same above the fusing point of the enamel at a temperature between 480° C. and 580° C.

2. The process of producing vitreous enamel coated aluminum-rich alloys having an improved enamel bond which comprises placing the alloy surface to be enameled in contact with an aqueous alkaline solution containing between 0.25% and 25% of a water-soluble chromate and having a temperature between 30° C. and the boiling temperature thereof for a period of between 1 and 30 minutes, heat-treating the chromate-treated alloy at a temperature between 350° C. and the heat tolerance limit of the alloy for a period of 2 to 10 minutes, and then enameling the so-treated surface with a vitreous enamel having a melting point below about 580° C. by applying said enamel to said heat-treated surface and fusing the same above the fusing point of the enamel at a temperature between 480° C. and 580° C.

3. The process of producing vitreous enamel coated aluminum-rich alloys having an improved enamel bond which comprises placing the alloy surface to be enameled in contact with an aqueous alkaline solution containing between 0.25% and 25% of a water-soluble chromate and having a temperature between 20° C. and the boiling temperature thereof for a period of one to thirty minutes, heat-treating the chromate-treated alloy at a temperature of 400° C. to 550° C. for a period of 2 to 10 minutes, and then enameling the so-treated surface with a vitreous enamel having a melting point below 510° C., the enamel being fired at a temperature between 480° C. and 510° C.

4. The process as defined in claim 2 in which the water-soluble chromate is an alkali metal chromate.

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#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

Number	Name	Date
1,230,958	Warga .....	June 26, 1917
1,971,240	Tosterud .....	Aug. 21, 1934

#### FOREIGN PATENTS

Number	Country	Date
273,956	Great Britain .....	July 14, 1927
463,790	Great Britain .....	Mar. 30, 1937