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PROCESS FOR ENAMELING ALUMINUM

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This invention relates to a process for producing porcelain or vitreous enamel coatings on aluminum. As used herein, the term "aluminum" includes aluminum of various grades and also aluminum base alloys. In particular the invention relates to a process employing steps of treating the aluminum in an acid solution and thereafter enameling, without necessarily employing a prefiring step.

United States Patents Nos. 2,467,114, 2,642,364 and 2,653,877 disclose enamel compositions and methods of performing the enameling step per se that may be employed in the process of this invention. The enamel compositions disclosed in these patents are particularly suitable for the enameling of aluminum, but the invention is not confined to the use of these compositions.

As has been pointed out in United States Patent No. 2,544,139, enameled aluminum has been successfully employed in many environments. However, in the presence of water or moisture, the enamels do not adhere tenaciously, particularly when applied to aluminum alloys. In fact, it is in connection with aluminum alloys, ordinarily desired for structural purposes, that adherence of enamels to the metal surface has been least satisfactory. The principal difficulty encountered is referred to as "water-spalling" and is evidenced by a flaking-off of the enamel.

Water-spalling of enameled aluminum has been reduced by employing the procedure described in the above-mentioned United States Patent No. 2,544,139, i. e. by immersing the aluminum in an aqueous alkaline solution of chromate, prefiring, and thereafter enameling. This procedure requires careful control of the solution composition and operating conditions for the alkaline chromate treatment, along with careful control of the prefiring step which is, of course, costly. Nevertheless, the procedure has not assured the production of enameled aluminum free from more than a reasonable number of failures attributable to water-spalling. In fact our experience with this procedure has been that failures are too often encountered, occasionally amounting to 50% of the material enameled.

Another procedure proposed for reducing water-spalling of enameled aluminum alloys includes a chemical treatment of the surface to be enameled in a phosphate-acid bath, also followed by a prefiring step prior to the enameling step. We have found, however, that the bath is rapidly exhausted and requires rather close control. Consequently, we have encountered failures with this procedure as well.

It is an object of this invention to provide a process for enameling aluminum by which enameled aluminum is obtained which is substantially free from water-spalling. It is a further object to provide such a process in which only simple control is required, particularly with respect to treating the aluminum surface prior to enameling. A particular object is to provide such a process in which the prefiring step heretofore deemed necessary

may be omitted. Other objects and advantages will appear in the ensuing description of the invention.

The invention consists in a process for producing an adherent porcelain or vitreous enamel coating on aluminum which is comprised of two main steps. In the first main step, after the usual cleaning step, the aluminum is treated in an aqueous acid solution containing chromic acid and sulfuric acid or chromic acid, sulfuric acid, and hydrofluoric acid. As an intermediate step, the aluminum may be prefired, if desired, by being heated for a few minutes at a temperature between 350° C. and the heat tolerance limit of the aluminum, but this step may be omitted with great economy and yet retain good adherence of the enamel. In the second main step, the alloy surface is enameled by applying and firing an enamel having a melting point below about 580° C.

For the first step the solution used contains, as its essential components, between 2 and 4 per cent by weight of chromic acid (CrO_3) and between 10 and 25 per cent sulfuric acid (H_2SO_4). We prefer, for silicon-containing aluminum alloys, that it also contain between 0.1 and 2 per cent of hydrofluoric acid (HF). A preferred, general purpose solution is one containing about 3.5 per cent chromic acid, about 17.5 per cent sulfuric acid, and about 1 per cent hydrofluoric acid, by weight. This solution can be made up with 35 grams of chromic acid, 175 grams of concentrated sulfuric acid, and 20 cc. of commercial (48%) hydrofluoric acid per liter.

This solution, or any solution in the range first given, is easily made up from the commercial acids; it is easily controlled within the limits given; and it does not, in fact, change materially with extended usage, except for some loss of hydrofluoric acid from solutions in which that acid is used. The aqueous acid solution is employed at a temperature between 70 and 100° C., preferably at about 80 to 90° C. The aluminum is treated by being immersed in the solution for a period between 1 and 5 minutes, preferably about 2 minutes. This treatment leaves no visible film or deposit on the aluminum but merely conditions the surface for the subsequent enameling step. This is in contrast to the treatment of aluminum in an alkaline chromate solution, which produces a film, said to be chromic oxide, on the aluminum surface, which film is said to be "fixed" by prefiring.

The aluminum so treated is enameled with any porcelain or vitreous enamel having a melting point below about 580° C. Best results have, however, been obtained by the use, at least for the first coat, of enamels of the type disclosed in the patents referred to at the beginning of the specification. Such enamels contain:

10 to 18 mole per cent PbO
38 to 65 mole per cent SiO_2
5 to 12 mole per cent Li_2O
0 to 22 mole per cent Na_2O
0 to 20 mole per cent K_2O, and
0 to 11 mole per cent TiO_2,

the total alkali metal oxide content

$$(Li_2O+Na_2O+K_2O)$$

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. However, ceramic pigments, refractory materials and other constituents also may be contained in the enamel composition.

In the enameling step, enamel is applied to the aluminum (by spraying on or dipping the aluminum in an aqueous slip and drying at low temperature, for example) and then fired above the fusing point of the enamel at

a temperature between 500 and 580° C., in some cases preferably at a temperature between 500 and 540° C., for a period between 2 and 30 minutes. Additional coats of enamel may be provided by repeating the enameling step.

I have found the process just described to be especially effective in the enameling of 61S aluminum alloy surfaces. It is equally useful and effective in the enameling of other aluminum surfaces, including the surfaces of aluminum alloys such as 3S, 52S and the casting alloy No. 43, for example. The alloying ingredients nominally contained in these aluminum alloys are tabulated below for convenient reference:

	Mn	Mg	Cu	Si	Fe	Zn	Cr	Ti
3S	1.25	------	0.2	0.6	0.7	0.1	------	------
52S	0.1	2.5	0.1	------	------	0.1	0.25	------
61S	0.15	1.0	0.3	0.6	0.7	0.2	0.25	0.15
43	0.3	0.05	0.1	5.3	0.8	0.2	------	0.2

The effectiveness of the process for producing an adherent enamel coating can, of course, be evaluated by means of the generally used water-spalling test which consists in immersing the test sample in 5 per cent ammonium chloride solution for 24 to 96 hours. Numerous specimens treated in accordance with the invention have been evaluated by use of this test and excellent performance in the test, with few or no failures, has been the uniform result, even when the prefiring step heretofore required was omitted.

As specific examples of the invention, numerous specimens of 61S aluminum alloy sheet were solvent cleaned and then immersed for 2 minutes at 80° C. in solutions composed of about 35 grams of chromic acid and 175 grams of concentrated sulfuric acid per liter, with and without about 20 cc. of commercial (48%) hydrofluoric acid per liter. The specimens were then removed from the acid solution, drained, and rinsed. The specimens were then sprayed with a slip of a ground coat of enamel within the composition range given above. For this purpose, Dupont's standard ground coat for 61S alloy, No. WB24 was used. The enamel so applied on the specimens was dried in a warm oven (temperature about 65° C.) and the enameled aluminum was then fired at a temperature between 500 and 540° C. for about 5′ and then cooled. The specimens were then sprayed with a slip of a cover coat of enamel within the composition range given above. For this purpose Dupont's typical black was used. The enamel so applied on the specimens was dried in a warm oven (temperature about 65° C.) and the enameled aluminum was then fired at a temperature between 500 and 540° C. for about 5′ and then cooled. The so-coated aluminum alloy specimens were tested in the ammonium chloride solution without failures.

It is understood that many different types of aqueous acid solutions have been used to etch or pickle aluminum surfaces for various purposes. With the particular solution referred to herein is effective in preventing water-spalling of enamels on aluminum is unknown. The combination of steps described herein, however, has been found most effective and easily employed.

We claim:

1. The process for producing an adherent enamel coating on aluminum which comprises treating the aluminum in an aqueous acid solution containing between 2 and 4 per cent by weight of chromic acid and between 10 and 25 per cent sulfuric acid, at a temperature of between 70 and 100° C., for a period between 1 and 5 minutes, and thereafter enameling the aluminum with an enamel having a melting point below about 580° C. by applying the enamel to the aluminum and firing the same above the fusing point of the enamel at a temperature between 500 and 580° C.

2. The process for producing an adherent enamel coating on aluminum which comprises treating the aluminum in an aqueous acid solution containing about 3.5 per cent by weight of chromic acid and about 17.5 per cent sulfuric acid, at a temperature of about 80 to 90° C., for a period of about 2 minutes, and thereafter enameling the aluminum with an enamel having a melting point below about 540° C. by applying the enamel to the aluminum and firing the same above the fusing point of the enamel at a temperature between 500 and 540° C.

3. The process for producing an adherent enamel coating on aluminum which comprises treating the aluminum in an aqueous acid solution containing between 2 and 4 per cent by weight of chromic acid, between 10 and 25 per cent sulfuric acid and between 0.1 and 2 per cent hydrofluoric acid, at a temperature of between 70 and 100° C., for a period between 1 and 5 minutes, and thereafter enameling the aluminum with an enamel having a melting point below about 580° C. by applying the enamel to the aluminum and firing the same above the fusing point of the enamel at a temperature between 500 and 580° C.

4. The process for producing an adherent enamel coating on aluminum which comprises treating the aluminum in an aqueous acid solution containing about 3.5 per cent by weight of chromic acid, about 17.5 per cent sulfuric acid and about 1 per cent hydrofluoric acid, at a temperature of about 80 to 90° C., for a period of about 2 minutes, and thereafter enameling the aluminum with an enamel having a melting point below about 540° C. by applying the enamel to the aluminum and firing the same above the fusing point of the enamel at a temperature between 500 and 540° C.

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