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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.

Heretofore various processes have been proposed for applying vitreous enamel coatings to aluminum. However, it has been found that the enamels do not adhere tenaciously to the metal surface particularly in the presence of water and moisture. In fact, it is in connection with aluminum alloys which are ordinarily desired for structural purposes that the adherence of the enamels to the metal surface has been least satisfactory. The particular difficulty encountered is referred to as "water-spalling" and is evidenced by a flaking off of the enamel.

Various methods of pretreating the metal have been proposed for reducing and overcoming this objectionable tendency.

One proposal involves immersing the aluminum in an aqueous alkaline solution of chromate, prefiring to temperatures between 350° and 600° F. 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 a 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.

Another procedure proposed for reducing water-spalling of enameled aluminum alloys and designed to eliminate the expensive time-consuming step of prefiring comprises treating the aluminum in an aqueous acid solution containing between 2 and 4% by weight of chromic acid and between 10 and 25% sulfuric acid, at a temperature of between 70 and 100° C., for a period between one and five minutes, and thereafter enameling the aluminum. While in some instances desirable results have been obtained by using this process, this process has not proved satisfactory without the imposition of a prefiring step between the treatment with the mixture of chromic acid and sulfuric acid and the enameling step. This is particularly true when relatively pure aluminum alloys such as 3S are being enameled.

Accordingly, it is an object of the present invention to provide a process for applying a vitreous enamel coating to aluminum.

It is a principal object of the invention to provide a process for enameling of aluminum which obviates the costly and hard to control step of prefiring. A still further object of the invention is the provision of a process which makes use of cheap, readily available materials and which can be easily controlled and may be carried out in a short period of time. It is also an objective of this invention to reduce the water-spalling tendency of enameled aluminum. Other objects and advantages will appear in the ensuing description of the invention.

These objects and advantages are achieved by the method of producing a non-water-spalling vitreous enamel coating on aluminum and aluminum alloys which comprises subjecting the metal surface to be enameled to a sequential series of operations to clean and pretreat said surface before applying and firing the enamel coating, said sequential operations comprising first subjecting said surface to the action of an aqueous alkali solution, thereafter subjecting said surface to the action of a deoxidizing solution capable of dissolving metallic oxides, and then forming a chromate conversion coating on said surface by subjecting it to the action of an aqueous acid solution containing hexavalent chromium ions and fluoride ions, rinsing the surface to remove the retreating solution, and thereafter applying the enamel to the thus treated surface and forming the vitreous enamel coating by fusing the enamel.

The invention therefore involves a process for producing an adherent porcelain or vitreous enamel coating which comprises four steps: cleaning, deoxidizing, chromate coating and enameling.

In the first operation, surface contamination such as dirt, grease, oils and the like, is removed by cleaning the surface with an alkali cleaning solution. During this operation the metal should be cleaned in such a manner as to avoid deeply etching the surface, since severe etching will lead to inferior adhesion of the enamel to the base metal. This can be accomplished by employing a mild alkali solution and preferably one containing an inhibitor such as trisodium phosphate which reduces the tendency of the alkali solution to dissolve and etch aluminum surfaces. Inhibited alkali solutions having a pH below 12 have been found to be particularly suitable for cleaning aluminum surfaces. Solvent cleaning of the metal is not suitable for the purposes of this invention. If a solvent cleaner is employed the results finally obtained will be markedly inferior to the vitreous enamel coatings formed on alkali cleaned surfaces.

After alkali cleaning, it is preferred to remove the residue of cleaning solution from the surface by means of a water rinse. This will tend to arrest the etching action of the alkali and also prevent "killing" the subsequently applied deoxidizing solution.

In the second step, the aluminum surface is deoxidized by removing metallic oxides adhering thereto. In general it has been found that any conventional deoxidizing solution for aluminum may be used in this step. However, in the process of the present invention it has been found that deoxidation can best be accomplished by means of dilute phosphoric acid, i. e., from 4 to 12% by volume of 75% phosphoric acid. If phosphoric acid is not used, other deoxidizing materials such as nitric acid and mixtures of nitric and chromic acid may be used. In general, the deoxidation treatment should also be of such a nature as not to severely etch the surface for the reasons given above in regard to step 1. After deoxidation, it is customary to rinse the deoxidized surface with water in order to remove any adhering deoxidizing solution, and prevent carrying it over into the chromate coating bath,

In the third step, the clean and deoxidized surface is subjected to the action of an acidic chromate coating solution containing hexavalent chromium ions and fluoride ions in proportions which produce a chromate conversion film on the surface. Such solutions and the application thereof are well known in the metal coating art and the solutions are sold commercially in the United States under various trade names such as "Alodine 600," "Alodine 1200," "Bonderite 710," "Iridite 14," etc. Additionally, solutions such as those disclosed in United States Patents, such as 2,276,353 and 2,507,956 are suitable for this operation.

After the chromate conversion coating has been formed on the surface of aluminum, it is essential to remove substantially all of the adhering coating solution from the surface before applying the enamel. In general, this removal may be done by thoroughly rinsing the coated surface with water. After removal of the adhering coating solution from the coated surface, it is also preferred that the surface be dried.

After drying, the surface may be coated with enamel which is applied and baked in accordance with the manufacturer's directions. United States Patents Nos. 2,467,-114, 2,642,364 and 2,653,877 disclosed 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 suitable for the enameling of aluminum, but the invention is not confined to the use of these specific compositions.

Obviously, if multicoats of enamel are to be applied, the second or third coat will be applied in the normal fashion.

As examples of how the new process may be carried out, the following non-limiting examples may be cited:

Formula No. I

	Pounds
Soda ash	0.35
Trisodium phosphate	0.55
Caustic soda	0.10
	1.00

Formula No. I is an excellent inhibited mild alkali cleaner which when dissolved in water to give a concentration of approximately 9 oz./gal. will clean aluminum in a power spray washer in from 5 to 7 seconds without imparting objectionable etch to the surface.

After cleaning the aluminum, it is customary to rinse the surface before deoxidizing so that the alkali will not be "dragged into" the deoxidizing bath of which the following is a typical example:

Formula No. II

	Gallons
75% phosphoric acid (H_3PO_4)	0.08
Water, to make 1.00 gallon.	

This solution when used as a spray at room temperature will deoxidize the average aluminum surface in less than 1 minute.

After deoxidizing the surface, adhering deoxidizing solution should be thoroughly rinsed from the surface with water. The clean deoxidized surface is then given a chromate conversion coating. Typical solutions for this purpose are:

Formula No. III

	Grams
Chromic acid	6
Ammonium fluosilicate	8
Water, to make 1 liter.	

Formula No. IV

Potassium dichromate	grams	18
30% fluosilicic acid	ml	20
Potassium ferricyanide	grams	5
Water, to make 1 liter.		

Formula No. V

	Grams
Chromic acid	5
Potassium ferricyanide	5
Barium fluosilicate	2
Water, to make 1 liter.	

Formula No. VI

48% hydrofluoric acid	ml	7
Ammonium dichromate	grams	100
Water, to make 1 liter.		

The chromate conversion coating may be formed from these solutions by subjecting the aluminum surface to the action of the solutions in the conventional and well known fashion, i. e., flowing, dipping, spraying, etc. After the coating is formed, residues of the coating solution are removed by thorough rinsing. After rinsing, the coated aluminum should preferably be dried.

The coated aluminum is enameled with any porcelain or vitreous enamel having a melting point below the melting point of aluminum and preferably those which form the enamel coat at temperatures below the heat tolerance of the metal, i. e., temperatures which will not adversely affect the strength of the metal. Best results have, however, been obtained by the use, at least for the first coat, of enamels containing lead, especially those of the type disclosed in the patents referred to above. Such enamels contain:

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

the total alkali metal oxide content

$$(Li_2O+Na_2O+K_2O)$$

of the enamel being between 25 and 36 mole percent, 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 in a conventional manner (by spraying on or dipping the aluminum in an aqueous slip and drying at low temperature, as 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.

It has been found that the process just described to be especially effective in the enameling of 3S aluminum alloy surfaces. It is useful and effective in the enameling of other aluminum surfaces, including the surfaces of aluminum alloys such as 52S and 61S. 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

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 percent ammonium chloride solution for 24 to 96 hours. Numerous specimens treated in accordance with the disclosure

given above have been evaluated in this test with few or no failures, even after 144 hours, thus clearly illustrating the advantages of the present invention.

We claim:

1. The method of applying vitreous enamel coatings to aluminum and aluminum alloys which comprises subjecting the metal surface to be enameled to a sequential series of operations to clean and pretreat said surface before applying and firing the enamel coating, said sequential operations comprising first subjecting said surface to the action of an aqueous alkali solution, thereafter subjecting said surface to the action of a deoxidizing solution capable of dissolving metallic oxides, and then forming a chromate conversion coating on said surface by subjecting it to the action of an aqueous acidic solution containing hexavalent chromium ions and fluoride ions, rinsing the surface to remove the treating solution, and thereafter applying the enamel to the thus treated surface and forming the vitreous enamel coating by fusing the enamel.

2. The method of applying vitreous enamel coatings to aluminum and aluminum alloys which comprises first subjecting the metal surface to be enameled to the action of a mild aqueous alkali solution containing an etch inhibitor, then treating said surface by subjecting it to the action of a dilute acid solution capable of dissolving metal oxides adhering to the metal surface without objectionably etching the metal, forming a chromate conversion coating on the thus treated surface by contacting the surface with an aqueous acidic solution containing hexavalent chromium ions and fluoride ions, rinsing the surface to remove the treating solution, and thereafter applying an enamel forming material to the thus treated surface and forming the vitreous enamel by fusing the enamel at elevated temperatures.

3. The method according to claim 2 wherein the metal surface is subjected to water rinses intermediate the various treatment steps prior to the application of the chromate conversion coating.

4. The method according to claim 2 wherein the metal, at all times prior to the application of the enamel forming material, is maintained at temperatures below the boiling point of the various treating solutions.

5. The method of applying vitreous enamel coatings to aluminum and aluminum alloys which comprises cleaning the metal surface to be enameled by subjecting it to the action of a mild alkali solution for a time sufficient to remove dirt and grease without objectionably etching the metal, rinsing the thus treated surface with water, subjecting the cleaned metal surface to the action of a deoxidizing solution having a deoxidizing action equivalent to that provided on treating the metal for less than one minute with an aqueous phosphoric acid solution containing from 4 to 12% by volume of 75% phosphoric acid, rinsing the thus treated surface with water, applying a chromate conversion coating by subjecting the thus treated metal surface to the action of an acidic aqueous solution containing hexavalent chromium ions and fluoride ions, rinsing the thus treated surface with water and thereafter applying an enamel forming material to the thus treated surface and forming the vitreous enamel coating by fusing the enamel forming material at elevated temperatures.

6. The method of applying vitreous enamel coatings to aluminum and aluminum alloys which comprises spraying the surface to be enameled with an aqueous solution containing 9 oz./gal. of a mixture of soda ash, trisodium phosphate and caustic soda (the weight percentage of such ingredients being 35%, 55% and 10% respectively) for 5 to 7 seconds, rinsing the thus treated surface with water, then spraying said surface with a phosphoric acid solution containing 0.08 gallon of 75% phosphoric acid in sufficient water to make 1 gallon of solution, rinsing the thus treated surface with water, applying a chromate conversion coating by subjecting the thus treated metal surface to the action of an acidic aqueous solution containing hexavalent chromium ions and fluoride ions, rinsing the thus treated surface with water and thereafter applying an enamel forming material to the thus treated surface and forming the vitreous enamel coating by fusing the enamel forming material at elevated temperatures.

7. In the process for producing vitreous enamel coating on aluminum and aluminum alloys involving cleaning the surface to be enameled to remove dirt, grease, oil and corrosion products, applying a chromate coating to the cleaned surface, prefiring the chromate coated material at elevated temperatures and thereafter enameling the chromate coated surface by applying thereto an enamel forming material which on firing at temperatures below the heat tolerance of the metal but above the fusing point of the enamel forms a vitreous enamel coating, the improvement whereby the prefiring of the chromate coated material can be eliminated, characterized in that cleaning the surface to be enameled by subjecting it to the action of an alkali solution containing an etch inhibitor, deoxidizing the cleaned surface by subjecting it to the action of a conventional aluminum deoxidizing solution, applying a chromate conversion coating to the cleaned deoxidized surface by subjecting it to the action of an aqueous acidic solution containing hexavalent chromium ions and fluoride ions, and rinsing and drying the thus treated surface.

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