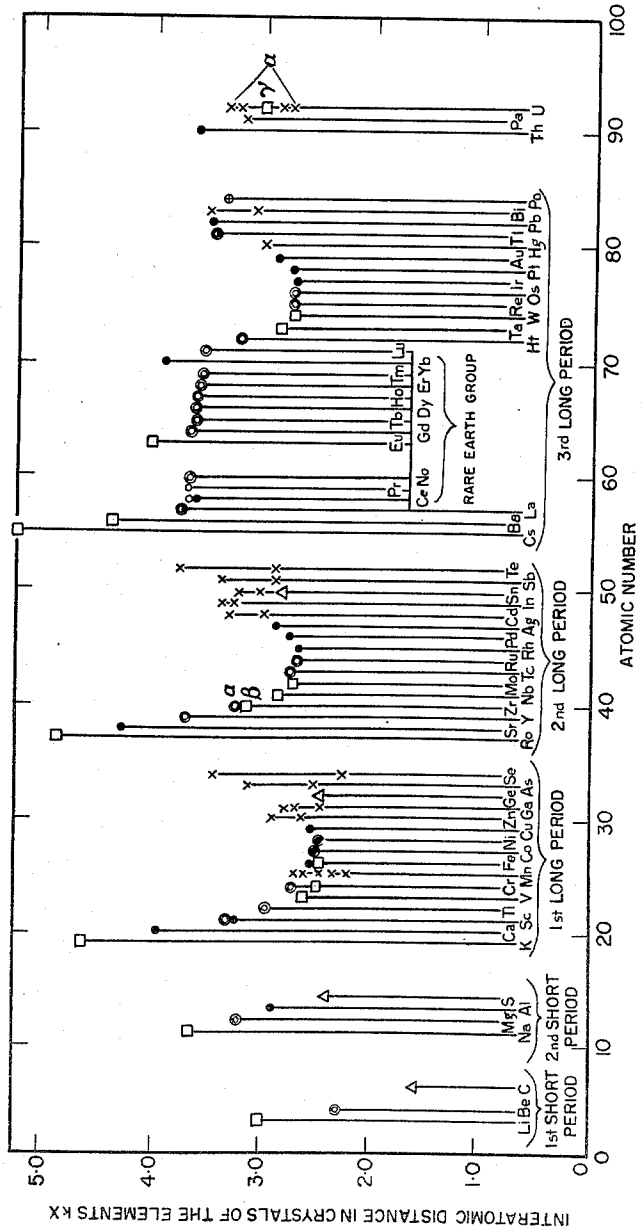
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ENAMELED ALUMINUM PRODUCTS AND METHODS OF MAKING THE SAME

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INVENTORS
Dean S. Hubbell
BY Ernest P. Weaver
J. Stanley Churchill
atty.

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ENAMELED ALUMINUM PRODUCTS AND METHODS OF MAKING THE SAME

Dean S. Hubbell and Ernest P. Weaver, Pittsburgh, Pa., assignors to H. H. Robertson Company, Pittsburgh, Pa., a corporation of Pennsylvania

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This invention relates to the enameling of aluminum and aluminum rich alloys with a vitreous enamel and more particularly to the enameled product and the method of enameling the aluminum and aluminum rich alloys.

One object of the invention is to provide a novel enameled product comprising aluminum and/or an aluminum rich alloy, enameled with a coating of a vitreous enamel and in which the enamel coating is tenaciously and permanently bonded to the aluminum and/or alloy by novel means to thereby render the enameled product suitable for a wide range of commercial and industrial purposes.

Another object of the invention is to provide a novel, simple and practical method of enameling aluminum and/or aluminum rich alloys with vitreous enamel for the production of an enameled product wherein the enamel coating is tenaciously and permanently bonded to a surface of the aluminum and/or alloy.

A still further object of the invention is to provide a novel and simple method by which a surface of aluminum and/or aluminum rich alloy may be pretreated to condition it for enameling with a vitreous enamel so that the enamel coating is caused to adhere to the surface of the aluminum and/or alloy with great tenacity.

With these general objects in view and such others as may hereinafter appear the invention consists in the enameled aluminum and/or enameled aluminum rich alloy; in the method of producing the same; in the method of pretreating the surface of the aluminum and/or aluminum rich alloy to condition the surface to enable it to be successfully enameled with a vitreous enamel; and also in the pretreated product thus produced.

The drawing is a chart to be referred to.

The present invention is concerned with the enameling with vitreous enamel of aluminum and/or aluminum rich alloys, that is alloys containing at least 80% by weight of aluminum and including the alloy which is commonly sold under the name of "commercially pure aluminum" and wherein the content by weight of aluminum approaches 99%.

Prior to the present invention extensive research has been conducted in the attempt to develop satisfactory commercial processes for the enameling of aluminum and aluminum rich alloys as above defined, and various proceses have been proposed for the pretreatment of the aluminum and aluminum rich alloys in the attempt to prdouce an enameled product in which the enamel coating adheres tenaciously to the aluminum and/or alloy surface. The most successful of such processes have involved the pretreatment of the aluminum and aluminum rich alloy with chromate solutions and the utilization of enameling frits of particular compositons. In practice

in all of such processes the many operations must be controlled within extremely narrow limits or tolerances.

As a result in practice the cost of such enameled aluminum products has been excessive, and the permanency of the bond between the enamel coating and the aluminum and/or alloy is always open to question particularly when exposed to the weather, and in many instances the commercial practice of these prior processes has been accompanied by a very substantial proportion of rejected enameled products unsuitable for commercial use and sale.

The present invention contemplates a method by which vitreous enameled aluminum and/or aluminum rich alloys may be produced at minimum expense and by a simple, practical and commercial method producing an enameled product in which the enamel coating adheres to the base metal with satisfactory tenacity. The invention contemplates a pretreatment of the surface of the aluminum and/or alloy in a manner such as to deposit thereon a bond promoting film which is believed to be metallic in nature, and which for purposes of description will be referred to as bond promoting material.

We have discovered after extensive research that certain of the metals which are grouped in the periodic table in the first and second long periods, together with some of the metals in the third long period appear to be capable of use in the present process of enameling for the deposition or production of the film of the bond promoting material. Our experience thus far has indicated that certain of the metals in such groups appear to be more suitable than others, as will be hereinafter pointed out.

We have also found out that in order to be suitable for the purposes of the present invention, the metals to be used for production of the bond promoting film on the surface of the aluminum or aluminum alloy must answer at least three requirements:

a. The metal must deposit out on the aluminum in a tightly adherent film;

b. It must be capable of diffusing into the aluminum alloy readily when subjected to heat treatment at temperatures below the softening temperature of the alloy;

c. Its oxide must fuse readily into the enamel without deterioration and preferably with improvement thereof.

From our work thus far we believe that the best adhesion between the aluminum or aluminum rich alloy and the bond promoting film results when crystal continuation occurs. This happens when the lattice parameters of the deposited metal are within 15% (either way) of those of the basis metal. Moreover the metals that fall within this plus or minus 15% variation in lattice parameters are those that diffuse most readily into the basis metal. Among the metals that meet the requirements of falling within this plus or minus 15% of lattice parameter and forming oxides that dissolve satisfactorily into the enamel, the best are the ones having the smallest atomic dimensions—(volume, diameter or interatomic distance). By plotting interatomic distances against atomic numbers, as illustrated in the drawing, it will be seen that most of the metals we have found to be most effective are found among the transitional elements in the first, second and third long periods and are near the minima of those portions of the curves.

The results of our research thus far have indicated that the metals having the atomic numbers 26, 41, 42, 51 and 73 gave the best results. These metals are respectively: iron, niobium, molybdenum, antimony and tantalum.

We have also discovered that the group of metals identified by atomic numbers 23, 25, 27, 28 and 74, and which comprise respectively the metals vanadium, manganese, cobalt, nickel and tungsten, have been found effective, but the first group is preferred.

The remaining metals with which we have experienced fairly satisfactory results include those identified by atomic numbers 22, 31, 33, 40, 45, 77, 81 and 90 and comprise respectively, titanium, gallium, arsenic, zirconium, rhodium, iridium, thallium and thorium.

The deposition of the bond promoting material may and preferably will be accomplished by simple immersion of the aluminum and/or alloy in a solution of such bond promoting material for a relatively short period of time until a film of the bond promoting material is deposited upon the surface of the aluminum and/or aluminum rich alloy. If found advantageous the deposition may be effected by spraying the solution on the aluminum or alloy, or in any other convenient manner. Thereafter the aluminum and/or aluminum rich alloy with its film of bond promoting material may be enameled with or without a prefiring and with a vitreous enamel composition which matures when fired at temperatures not substantially exceeding the softening temperatures of the particular aluminum and/or aluminum rich alloy which is being enameled.

It has heretofore been generally recognized that commercially pure aluminum articles may be enameled with vitreous enamel without requiring pretreatment. These commercially pure aluminums had a purity approaching about 99% aluminum, and fairly satisfactory results have been obtained following known procedures in the application of the commercial compositions of vitreous enamel which may be fired and matured at temperatures of around 980° F. which approaches the softening temperature at which the aluminum article is deteriorated. Experience has shown that various commercial aluminum rich alloys, and particularly those which are heat-hardening alloys, have presented serious difficulty in producing a tenaciously adhering enamel coating when the attempt was made to enamel them following prior procedures. While, as above stated, commercial aluminum contains about 99% aluminum, the commercial aluminum rich alloys contain from slightly greater than 1% to 20% of various alloy elements including, for example, manganese, zinc, copper, chromium and silicon. The fact that the vitreous enamel coating does not adhere with satisfactory tenacity to these aluminum rich alloys has presented problems for the satisfactory use of the enameled aluminum article, particularly when exposed for long periods of time to weathering and to moisture laden atmosphere. The phenomenon referred to as "water spalling" is often experienced and accompanied by a flaking off of the enamel, exposing the underlying bare metal. Usually this "water spalling" starts at the edges of the enameled articles, or at pin holes, or any other slight flaws in the enamel coating. The "water spalling" appears to be a progressive action and may result in minor failure or or even in complete failure if sufficient time elapses for the spalling process to continue. In any event the problem of providing aluminum rich alloys of a satisfactory, tightly bonded vitreous enamel has proven troublesome of solution, and as far as we are aware the most satisfactory process for the production of such a product is that developed by the Du Pont Company and following the subject matter generally of United States Patent No. 2,544,139. As disclosed in such patent, this prior process contemplates the pretreatment of the aluminum alloy with chromate solutions and the maintenance of exceedingly closely controlled operating conditions in order to produce a satisfactory enameled aluminum rich alloy.

In general the aluminum alloys with which we have experimented and which have presented substantial difficulty in enameling with a vitreous enamel include the alloys and compositions in the following table:

Aluminum Assn. Designation	Member of Group Tested	Old Designation	Chemical Composition
1XXX-----	1100	2S	1.0% Si, Trace Fe, 0.2 Cu, 0.05 Mn, 0.10 Zn.
Al—99% minimum. Pretreatment unnecessary, but is completely annealed during enameling			
2XXX-----	2024	24S	0.5 Si, 0.5 Fe, 3.8 to 4.9 Cu, 0.3 to 0.9 Mn, 1.2 to 1.8 Mg, 0.1 Cr, 0.25 Zn.
Cu is major alloying element. Pretreatment necessary			
3XXX-----	3003	3S	0.6 Si, 0.7 Fe, 0.2 Cu, 1.0 to 1.5 Mn, 0.1 Zn.
Mn is major alloying element. Pretreatment unnecessary, but is completely annealed during enameling			
4XXX-----	4343	44S	6.8 to 8.2 Si, 0.8 Fe, 0.25 Cu, 0.10 Mn, 0.2 Zn.
Si is major alloying element. Pretreatment unnecessary, but results are improved by pretreatment			
5XXX-----	5052	52S	.45 Si, Trace Fe, .10 Cu, .10 Mn, 2.2 to 2.8 Mg, .15 to .35 Cr, .20 Zn.
Mg is major alloying element. Pretreatment necessary			
6XXX-----	6061	61S	.4 to .8 Si, .7 Fe, .15 to .40 Cu, .15 Mn, .8 to 1.2 Mg, .15 to .35 Cr, .25 Zn, .15 Ti.
Mg and Si major alloying elements. Pretreatment necessary. Is heat hardened by enameling			
7XXX-----	7072	72S	.7 Si, Trace Fe, .1 Cu, .1 Mn, .1 Mg, .8 to 1.3 Zn.
Zn is major alloying element. Pretreatment necessary			

The foregoing are typical of the many different classes of aluminum rich alloys and the nomenclature is that developed by The Aluminum Association for wrought aluminum and aluminum alloy products.

As above stated, we have discovered that the solution to the problems above indicated involves the pre-treatment of the aluminum rich alloys with solutions of the bond promoting material and preferably the bond promoting materials indicated by atomic numbers 26, 41, 42, 51 and 73 above referred to. In some instances, as above indicated, this may be accomplished by simple immersion of the aluminum and/or aluminum alloy in the solution, either acid or alkaline, of a compound or salt of such bond promoting material or by spraying the solution on the aluminum or alloy or in any other convenient manner, including the deposition from the vapor phase, and as a result of such treatment an extremely thin coating or film of the bond promoting material may be produced on the aluminum or aluminum rich alloy. This is followed by the subsequent enameling of the same with any usual or preferred composition of those frits which are available on the market having maturing temperatures near and preferably slightly below the temperatures at which the aluminum or aluminum alloys soften and sag. Generally speaking, such frits have maturing temperatures at or about 980° F. and have as their foundation a lead borosilicate glass. In practice we have experienced satisfactory results in the application of various commer-

cial compositions of such frits including, for example, the following:

Ground Coat—
100 pounds ground coat frit #01261
4 pounds #1133 medium
11 pounds 11 oz. milling compound #0885
Specific gravity, 1.9 to 2.4. Grind 0–1% on 325 mesh screen

Cover coat—
100 pounds cover coat frit #01262
5 pounds opacifier #0886 (TiO_2)
5 pounds 9 ounces green oxide #0887 (Cr_2O_3)
4 pounds 6½ ounces #1133 med. (alcohol)
27 pounds 10 ounces water
Grind 0–1% on 325 mesh screen. Specific gravity, 1.9–2.0

Cover coat, used directly on aluminum, no ground coat—
100 pounds cover coat frit #01262
5 pounds 9 ounces opacifier #0886
5 pounds 8 ounces green oxide #0887
4 pounds medium #1133
7 pounds milling compound #0885 (silicate)
27 pounds 10 ounces water
Grind to 0–1% on 325. Specific gravity, 1.98

The above three formulations are manufactured by the O'Hommel Company, Carnegie, Pennsylvania

Cover coat, direct to aluminum—
5 pounds frit AL–617
170 gms. milling compound #AD–1
113 gms. opacifier
113 gms. green oxide #0887
680 gms. water
Grind 0–1 gm. on 325. Specific gravity, 1.9

This is manufactured by Pemco, Baltimore, Maryland

Cover coat, direct on aluminum—
1200 gms. frit #AL–2
90 gms. milling compound #L–389
36 gms. green oxide #3630
360 gms. water
Grind to 0–1 gm. on 325. Specific gravity, 1.9

This is manufactured by Ferro Corporation, Cleveland, Ohio

If desired, any of the frit compositions disclosed in United States Patent No. 2,467,114 may be used, and any of the other known compositions of frits recommended as suitable for enameling aluminum and having the required maturing temperatures may be used.

The procedure recommended to be followed involves the following five steps:

1. Cleaning
2. Pretreatment
3. Prefiring, in some instances not necessary
4. Application of slip
5. Firing

The procedure to be followed in steps 1, 3, 4 and 5 may and preferably will be similar to the practice which is followed in the present prior art enameling processes as applied to aluminum. It is understood that a clean surface is required, and in practice this may involve solvent cleaning, either in the liquid or vapor phase, followed in some instances by subsequent immersion in a 6% sulphuric acid solution to which a detergent has been added. This is followed by a water rinse so that the surface of the aluminum rich alloy is rendered free of oil, excessive oxide and the like.

The prefiring step involves the subjecting of the pretreated and rinsed sheet for a short period of time, as for example, 3 or 4 minutes to a temperature of 1000° F., or at least to the approximate temperature at which the enamel will be subsequently fired, and generally this prefiring step has been found desirable and it is to be recommended although satisfactory results in many instances have been obtained without prefiring. Prefiring at 1000° F. is preferred. The preparation and the application of the frit and its firing follows common practice and at the temperatures recommended to insure maturing of the frit, and our experience indicated that the pretreatment, as hereinafter described, permits a one-coat application as well as the application of several coats, such as the application of a ground coat followed by one or two "color" or "cover" coats. When a one-coat application is to be made the slip is adjusted or modified by appropriate "mill additions" to suit it for direct application to the pretreated aluminum surface.

The pretreatment of the surface of the aluminum or aluminum rich alloy consists of chemically precipitating or "flashing" a light deposit of the bond promoting material above described onto the surface of the aluminum or its alloy, preferably from an alkaline solution thereof. For example, solutions containing about 6.4 gms. of Sb_2O_3 per liter; about 8 gms. of NaOH per liter; to which if desired about 4 gms. of ammonium sulfamate per liter may be used. Analysis of the film deposited on alloy 61S showed variations in amount of antimony ranging from .022 gm. per sq. ft. to 0.106 gm. per sq. ft. when no prefiring was employed. When prefired after the antimony flash the amounts of antimony ranged from .020 to .058 gm. per sq. ft. The variations depended on the length of immersion of from 1 to 10 minutes.

If desired, acid solutions of antimony may be used, such as 3.8 parts Sb_2O_3; 24 parts H_2SO_4 and 1000 parts of H_2O. Sodium carbonate (Na_2CO_3) may be used with advantage instead of sodium hydroxide (NaOH) and in amounts corresponding to and equivalent of the NaOH. When the carbonate is used, the action is slower and heating the solution to about 170° is recommended. This procedure has the advantage of enabling accurate control of operating temperatures to be maintained and has a second advantage in that it avoids the production of excessive hydrogen on the metal so that the prefiring step before enameling may be omitted. When those metals of the above set forth groups of materials are used in alkaline baths and which tend to cause the formation of troublesome curds and precipitates we have found that a "chelating" agent, such as ethylene diamine tetra acetic acid may be used to overcome this difficulty. Iron and manganese are typical of the troublesome metals. Instead of adding the tetra acetic acid to the iron or manganese solution, we may prefer to form the bath using the iron or manganese salt available on the market under the trade names "Perma Green Manganese" and "Perma Green Iron."

30 gm. Perma Green (iron or manganese)
83.2 gm. NaOH
3 liters water

We have also found that the step of prefiring is not absolutely necessary but generally desirable. A uniformly thin, tightly adherent film of the bond promoting material is sought. Prefiring assures this because it disposes of excess, loosely adherent material by causing it to volatize away and the remaining material to become anchored to the aluminum by at least partial diffusion into it. If the bond promoting material is applied by precipitation from solution, prefiring of the deposited film is preferred. It is possible, however, to eliminate the step of prefiring if the bond promoting material is deposited in a uniform, tightly adherent thin film. This can be accomplished by closely controlling solution strengths, temperatures and times of immersion.

As above pointed out, the prefiring step may be eliminated by the use of the sodium carbonate (Na_2CO_3) bath, and in addition we have found that when niobium (columbium) either alone or in the commercially available mixture with tantalum is used as the bond promoting material, it is recommended that the step of prefiring be

eliminated. The following is a typical formulation which may be used:

10 gms. mixture of tantalum-niobium oxide
300 cc. NH_4OH
100 gms. NaOH
3 liters H_2O

It is recommended that the immersion of the base metal into the bath be continued for about five minutes and that the bath be heated to about 100° F.

A valuable contribution resulting from use of the bond promoting material is the greater latitude in "shop variables" that may be tolerated without harmful effect on adhesion of the enamel. For example, we have found that an appreciably longer period of days may elapse between the grinding and use of commercial frits. Also it is less important to fire the "bisque" while it is still wet. Considerably greater variations in immersion times, temperatures and concentrations of the pretreatment solution can be tolerated. Greater variations can be tolerated in the temperature at which the enamel is fired. Moreover, the pretreatment solutions are less quickly depleted and remain effective over longer periods of use than those in prior use.

If found advantageous, the deposition of the bond promoting material may be effected from the vapor phase by introducing the aluminum or aluminum rich alloy in an atmosphere containing the material. Such atmospheres may be readily produced by heating a compound of the material with controlled access of air. In the case of antimony we prefer to use antimony sulfide or stibnite, and in this instance three volumes of sulfur dioxide are produced along with each volume of the antimony trioxide. The presence of the SO_2 appears to be of benefit.

In practice we heat the sheet of aluminum alloy to approximately 980° F. and then move it into a zone of the furnace where it is exposed to the fumes given off from stibnite that has been heated with a controlled supply of air. These fumes immediately deposit out in a uniform, tightly adherent layer on the surface of the hot sheet and immediately diffuse into the aluminum. After an interval (ranging from 1 minute to 10 minutes) the aluminum alloy sheet is removed from the furnace and allowed to cool in air. It is then given a spray or dip rinse in dilute sodium hydroxide (approximately 2.5 gms./liter) followed by clear water. It is then ready for the application of frit without further treatment.

In some instances we have experienced particularly good results by the introduction of a small amount of water vapor in the form of steam which is introduced into the furnace with the air. The deposition of the antimony appears to produce a golden surface on the aluminum or aluminum alloy sheet, and this appearance has accompanied the production of the most desirable and tightly adhering enamel coatings on the sheets.

In addition to its utility in promoting the tenacity with which vitreous enamel coatings may be caused to adhere to the aluminum and aluminum rich alloys, we have found that the treatment with the bond promoting material, as above described, produces a character of surface in the aluminum or aluminum alloy to which other coatings, such as organic coatings, also adhere with greater tenacity. The aluminum and aluminum alloy coated with these bond promoting metals also possess more attractive appearances after weather exposure.

The individual elements comprising the different groups above referred to may be used alone or mixed with others of said groups as bond promoting materials. For example, niobium and tantalum occur together, and we have found it unnecessary to go to the trouble and expense of separating them.

The present invention may also be used with advantage in enameling aluminized steel. In this instance the aluminum coating over the steel being supported by the steel relaxes the limitations as to the maturing temperature of the frit, so that it is possible to utilize those frits which mature nearer the melting point of aluminum.

From the foregoing it will be apparent that the present invention provides a simple, efficient and practical method of enameling aluminum and those aluminum rich alloys which have heretofore presented great difficulty. The process lends itself to commercial operation because of its simplicity and because of the relatively wide tolerances permitted in the various operations.

This application is a continuation-in-part of our copending application, Serial No. 500,988, filed April 12, 1955, now abandoned.

Having thus described the invention, what is claimed is:

1. The method of enameling a surface of an article, said surface consisting of an aluminum alloy selected from the group consisting of alloys identified as 2XXX, 4XXX, 5XXX, 6XXX and 7XXX, comprising contacting a clean surface of said article with an aqueous alkaline solution of antimony oxide, terminating said contact after a thin film of bond promoting material containing antimony has been deposited on said surface, heating the film covered article to a temperature of about 1000° F. for a short period of time and cooling the article containing from 0.02 to 0.058 gram of antimony per square foot of said surface, applying to said surface thus treated a vitreous enameling frit having a maturing temperature less than the melting point of said alloy, and firing the fritted article to mature the frit and to form a tightly and permanently bonded vitreous enamel coating over said surface.

2. The method of claim 1 in which said alkaline solution comprises approximately 6.4 parts by weight of antimony trioxide, 8 parts by weight of sodium hydroxide and 985.6 parts by weight of water.

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