April 12, 1960 D. S. HUBBELL ET AL 2,932,584

ENAMELING OF ALUMINUM ALLOYS

Filed Feb. 28, 1958 2 Sheets-Sheet 1

Fig. 1.

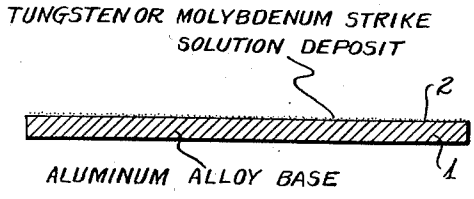
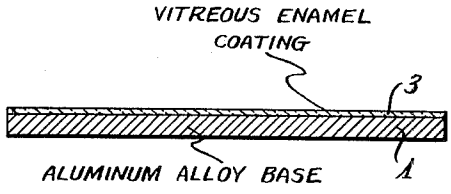


Fig. 2.



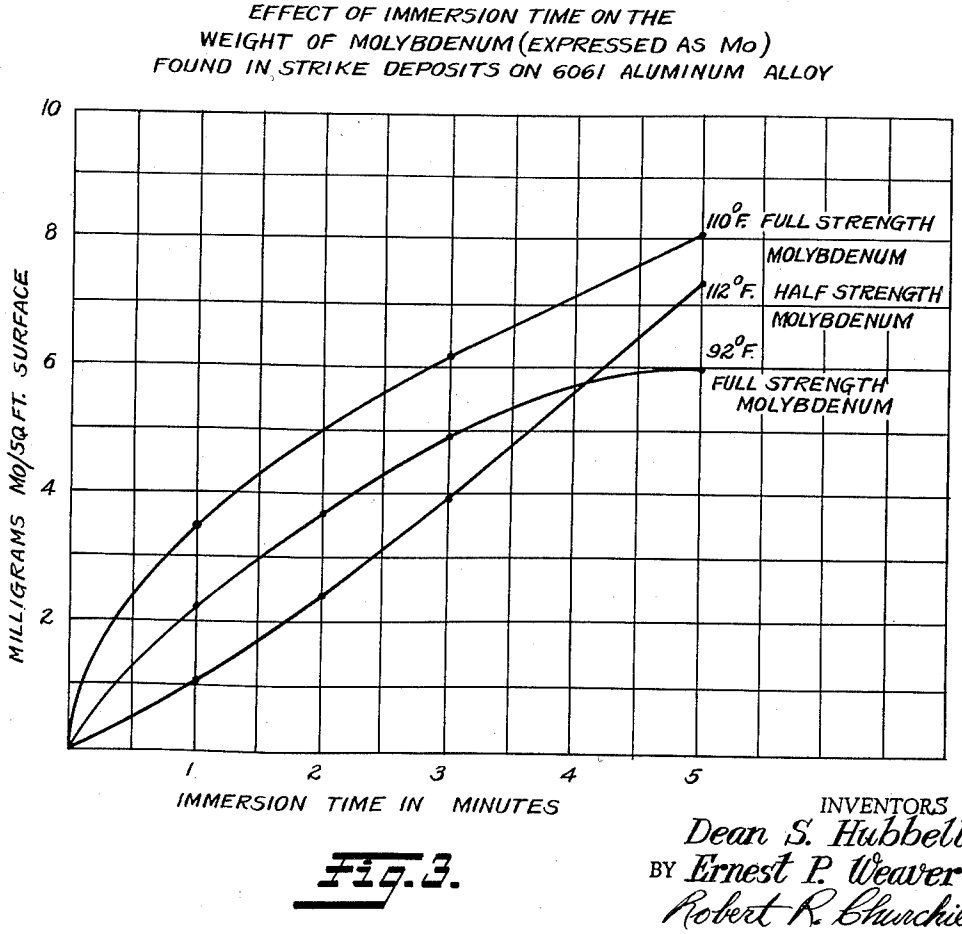


Fig. 3.

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ENAMELING OF ALUMINUM ALLOYS

Filed Feb. 28, 1958 2 Sheets-Sheet 2

EFFECT OF ALKALINITY OF STRIKE SOLUTION ON THE WEIGHT OF MOLYBDENUM (EXPRESSED AS Mo) FOUND IN STRIKE DEPOSITS ON 6061 ALUMINUM ALLOY

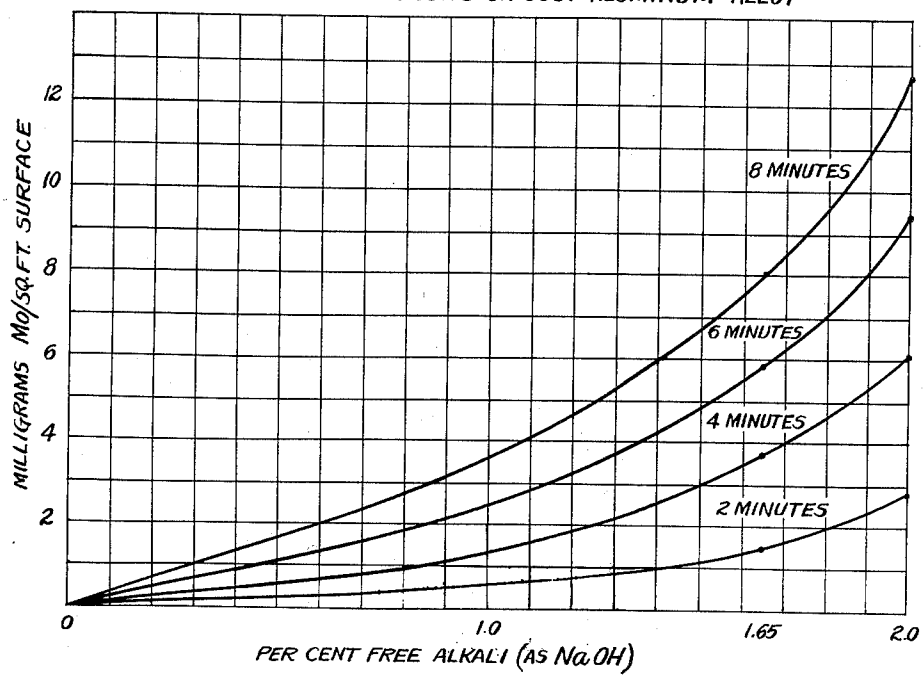


Fig. 4.

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ENAMELING OF ALUMINUM ALLOYS

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Application February 28, 1958, Serial No. 718,176

26 Claims. (Cl. 117—53)

The present invention relates to the enameling of aluminum with a vitreous enamel, and more particularly to the enameling of aluminum alloys containing magnesium and silicon as the most significant alloying elements.

There has been increased interest in recent years in the use of vitreous enameled aluminum structural elements, particularly in sheet form as a building skin. For this purpose, it is necessary that a hardenable alloy of aluminum be employed so that the finished product will have the desired structural strength.

There are two types of hardenable aluminum alloys. One of these is the work-hardening type which is received in a tempered or hardened condition which it has attained as a result of cold reduction, etc. This temper would, however, be lost during enameling because the firing temperature of the vitreous enamels used, which is in the neighborhood of 1000° F., completely anneals the alloy.

It is obvious, therefore, that the vitreous enameled articles with which the present invention is concerned, should be heat-hardening alloys. Wrought articles of these alloys may be received in a non-hardened condition, and will be hardened or tempered during the firing of the vitreous enamel which has been applied thereto in the form of a slip. All of the known heat-hardening alloys of aluminum are not, however, suitable for enameling to produce structural elements. For example, certain types of heat-hardening alloys contain considerable amounts of copper and soften at a temperature too close to the maturing temperature of currently available enamels used commercially.

The most suitable of the heat-hardening alloys of aluminum for use in manufacturing vitreous enameled sheets for structural purposes, from the standpoint of strength, workability, and corrosion resistance as well as from the standpoint of obtaining a suitable temper as a result of the firing of the enamel slip, are those in which magnesium and silicon are the principal alloying elements. This type of alloy has been called the "magnesium-silicon" series of aluminum alloys by The Aluminum Association and given a numerical designation as the 6XXX series. For convenience, they will be referred to hereinafter by their numerical designation. One member of the series which is particularly suitable, an alloy designated 6061, contains the following percentages of alloying elements: Silicon, .4 to .8; iron, .7; copper, .15 to .4; manganese, .15; magnesium, .8 to 1.2; chromium, .15 to .35; zinc, .25; and titanium, .15.

Another alloy, 6063, which is frequently used for extrusions contains the following percentage of alloying elements: Silicon, 0.20 to 0.60; iron, 0.35; copper, 0.10; manganese, 0.10; magnesium, 0.45 to 0.90; chromium, 0.10; zinc, 0.10; titanium, 0.10.

The 6XXX series of aluminum alloys, however, presents great problems as regards the application of a vitreous enamel. Unlike the so-called "commercially pure" aluminum and certain of the work-hardening alloys which can be enameled with ease after simple surface cleaning operations, all of the usual procedures fail to provide a tight and permanently adherent coating when an aluminum alloy of the 6XXX series is enameled. These alloys

may fail to produce a tight bond with the vitreous enamel coating from the outset, or, even when a tight, adherent bond has apparently been obtained, they may develop defects months or even years later when the enameled product is subjected to weathering. This delayed phenomenon is known as water-spall, and is probably due to the delayed hydration of magnesium oxide that formed at the interface during the enameling operation. Fortunately, it is possible to determine if this delayed spall will occur by immersing the enameled article in a 5% ammonum chloride solution for a period of 1 to 4 days. Experience has shown that specimens that do not spall in such a test will not spall in the weather.

It is believed that magnesium is the principal culprit in the enameling of alloys of the 6XXX series, probably because of the formation of basic magnesium compounds and magnesium-alumino-silicates at the metal-enamel interface. These are gelatinous compounds, and yield products which, during firing, will not migrate into the base metal or dissolve into the molten enamel. Instead, they are converted to a particularly reactive form of magnesium oxide. It has been found that in general, the greater the ratio of magnesium to silicon, the greater is the difficulty experienced on attempting to enamel the alloys employing conventional practices. It is obvious that it will not always be sufficient to clean the aluminum alloy surface to remove all magnesium compounds prior to enameling, since the enamel slip, itself, is an aqueous alkaline solution, and thus could cause the undesirable magnesium compounds to again be formed.

In the preferred members of the 6XXX series, the alloys designated 6061 and 6063, the Mg/Si ratio is usually less than the critical value, 1.73, which corresponds to dimagnesium silicide, Mg_2Si. It is sometimes possible to enamel these alloys without pretreatment other than adequate cleaning, with apparent success. However, the assurance that the enameled product will be free of water-spall on exposure to the elements for extended periods is not sufficient to make such practice commercially attractive. If the Mg/Si ratio exceeds 1.73 to such an extent that there is an appreciable excess of magnesium above the amount that can combine with the silicon to form Mg_2Si, the alloy is not considered suitable for enameling.

Several processes have been proposed for enameling the 6XXX alloys, but none has been particularly successful from the commercial standpoint. They have either required expensive and time-consuming steps, such as prefiring, unduly close control of the several operations involved, or have, in actual production, produced such erratic results that costs have been high and permanency of the bond placed in doubt.

Accordingly, it is the primary object of the present invention to provide a process for the vitreous enameling of articles composed of an aluminum alloy of the 6XXX series, which process produces a vitreous coating that is tenaciously bonded to a surface of the alloy and remains so bonded even after long exposure to the weather.

Another object of the present invention is to provide a process for the enameling of 6XXX aluminum alloy articles which does not require a prefiring of the article prior to application of the vitreous coating.

A further object of the present invention is to provide a process for the enameling of 6XXX aluminum alloy articles in which a moist enamel slip may be allowed to dry slowly to complete dryness on the surface of the article prior to firing.

Still another object of the present invention is to provide a process for enameling 6XXX aluminum alloy articles in which a colored "cover coat" may be applied directly to the metal, eliminating the usual "grip coat."

Yet another object of the present invention is to pro-

vide a process for enameling 6XXX aluminum alloy articles which avoids the difficulties ordinarily arising from the use of over-alkaline enamel slips.

Another and further object of the present invention is to provide a process for enameling 6XXX aluminum alloy articles which permits acceptance of the full range of tempers of this type of alloy without variations in procedure.

A still further object of the present invention is to provide a process for the enameling of 6XXX aluminum alloy articles which is simple, economical in operation, and produces uniform results.

Another object of the present invention is to provide a process for pretreating the surface of 6XXX aluminum alloy articles so that a surface of the article may easily be coated with a vitreous enamel which will tenaciously and permanently adhere to the surface.

Still another object of the present invention is to provide a 6XXX aluminum alloy article having a surface pretreated so that it may be coated with a vitreous enamel which will be tenaciously and permanently bonded thereto.

Yet another object of the present invention is to provide an enameled 6XXX aluminum alloy article in which the vitreous enamel coating is tightly and permanently bonded to the surface of the article.

Other and further objects of the invention will be apparent from the following detailed description taken in conjunction with the drawings in which:

Fig. 1 illustrates diagrammatically a 6XXX aluminum alloy article, a surface of which has been pretreated according to the present invention;

Fig. 2 illustrates diagrammatically a 6XXX aluminum alloy article which has been enameled according to the present invention; and

Figs. 3 and 4 are graphs showing the effect of varying the conditions of the present invention.

We find that 6XXX aluminum alloy articles may readily be enameled with a conventional frit for the vitreous enameling of aluminum to provide a tightly and permanently adherent coating if the surface of the alloy to be enameled is treated prior to the application of the vitreous composition, with a "strike solution" having a particular composition. This strike solution is an alkaline solution of molybdic or tungstic oxides and a chelating agent.

The exact role which this treatment plays in the enameling operation is not known. It is known that a solution of alkali, alone, will deposit a "smut," largely amorphous in character, on the surface of both "commerically pure" aluminum and the heat-hardening 6XXX aluminum alloys, and it may be assumed that this or a similar smut would be produced by the moist enamel slip. The following table is a comparison of the smuts obtained on the surface of "commercially pure" aluminum and the aluminum alloy designated "6061," the approximate percentages of the various elements (not necessarily present in elemental form) being obtained by spectrographic analysis:

TABLE I

Composition of "smut" deposited by alkali on "commercially pure" aluminum and on 6061

	Commercially Pure Aluminum, Percent by weight	6061, Percent by weight
Silicon	1.0	10
Iron	10	>10
Copper	1.0	10
Manganese	1.0	>10
Magnesium	0.1	10
Chromium		10
Zinc		>1
Titanium	1.0	0.3
Aluminum	10	10

Commercially pure aluminum presents no difficulty on enameling, but, as pointed out earlier, difficulty, at least in the form of water spall, is usually encountered in the enameling of the 6061 alloy, if conventional procedures are used. As also stated earlier, it is believed that the presence of appreciable amounts of magnesium is the principal reason that this difficulty is encountered.

If a clean surface of 6061 alloy is treated prior to enameling with the molybdenum strike solution, which will be described in greater detail hereinafter, there is obtained a surface deposit which by spectrographic analysis can be shown to contain the elements in the approximate percentages given in the following table:

TABLE II

Composition of film deposited on "6061" upon treatment with alkaline molybdenum

	Percent by weight
Silicon	13.5
Iron	13
Copper	6.5
Manganese	1.0
Magnesium	23.0
Chromium	6.0
Zinc	<1.0
Titanium	1.0
Aluminum	27.0
Molybdenum	8.0

From this it will be seen from the amount of magnesium, calculated on the basis of its elemental form, present in the deposit from the strike solution as compared with the amount in the smut produced by a solution of alkali, alone, that the success of the present invention does not depend on the elimination of magnesium. The fact that the alloy article having its surface treated with the molybdenum strike solution can easily be enameled, whereas that treated with an aqueous solution of alkali, alone, cannot, indicates that either the magnesium is present in a different form in the strike deposit, or that molybdenum is present in such a form that good adhesion is promoted. Probably both are true.

We have found, for example, that when dimagnesium silicide, Mg_2Si, is placed in a dilute solution of sodium hydroxide, a cloudy white precipitate forms, presumably at least partially magnesium hydroxide. If the caustic solution contains a chelating agent of the type to be described hereinafter, the precipitate is noticeably less, but still present. However, if the solution contains both the chelating agent and molybdic oxide, the solution remains clear when dimagnesium silicide is added. Also, it has been noted that when a soluble aluminate and a soluble silicate are mixed, the resulting solution forms a stiff gel. The formation of this gel can be prevented by the presence of both the chelating agent and molybdic oxide, but not by either alone. These observations seem to indicate that the presence in the strike solution of a chelating agent and molybdic oxide or tungstic oxide (which acts in the same manner as molybdic oxide) would prevent magnesium compounds of a troublesome nature, such as magnesium alumino-silicate, from being formed at the alloy surface.

As to the role of molybdenum actually present in the strike deposit, it is believed that it does not deposit directly on the aluminum alloy surface. It is believed that the smut first forms on the alloy surface and that this smut then absorbs a molybdenum compound from the strike solution by a mechanism similar to that by which dyes are taken up in similar amorphous films or smuts on aluminum. Metallic molybdenum is not present as such in the strike deposit, and the molybdenum is undoubtedly there in combined form as a salt. On firing of the enamel slip, this is converted to molybdic oxide which promotes the solution of the various ingredients of the strike deposit into the molten vitreous

layer, thereby bonding the vitreous enamel tightly to the alloy surface.

The strike solution will, therefore, comprise an aqueous solution of an alkali metal hydroxide, molybdic oxide, MoO_3, or tungstic oxide, WO_3, and a chelating agent. Borax is preferably added to contribute to the free rinsing of an article treated with the solution, but this material is not believed to be an essential ingredient of the solution. The relative proportions of the various ingredients are not critical, and may be varied within rather wide limits, depending on the time of contact of the solution with the article surface and the temperature of the solution, as will be explained in greater detail hereinafter.

Sodium hydroxide, because of its cheapness and ready availability, is preferred as the material to be used to give the required alkalinity, but any alkali metal compound which will furnish in aqueous solution free alkali within the range of 0.8 to 2.5% by weight, preferably about 1.2% by weight, may be used.

Molybdic oxide or tungstic oxide may be used interchangeably in the present process, and may be used singly or in admixture. Molybdic oxide is, however, preferred from the standpoint of economy.

It will be understood, of course, that while for purposes of convenience the molybdenum and tungsten contents of the strike solutions are referred to in terms of their oxides, these materials do not exist as such when dissolved in the alkaline solution. Also, it will be understood that any soluble form of molybdenum or tungsten may be employed to form the strike solution so long as the resulting solution has the free alkali content set forth above.

The amount of molybdic oxide or tungstic oxide in the strike solution may in particular be varied over a wide range. It will be recalled, in this regard, that the deposition of molybdenum or tungsten compounds on the alloy surface is not the result of a primary reaction of the treating solution. Rather, it is believed that it is absorbed by a so-called "smut" which is first formed on the surface of the alloy. Probably the best way to express the amount of molybdenum or tungsten which is to be present in the strike solution is in terms of that necessary under the conditions existing at the time of a particular treating operation to deposit on the article being treated 1 mg. to 12 mg. of the element per square foot of surface, with a deposition of 2 mg. to 6 mg. being preferred.

In other words, the factors of molybdenum or tungsten content, contact time, solution temperature, and alkalinity of the treating solution, all exert a pronounced effect on the molybdenum or tungsten content of the strike deposit.

Figure 3 of the drawings illustrates graphically the effect of the immersion time of the article in the strike solution, on the weight of molybdenum (expressed as Mo) present in a strike deposit on 6061 alloy when employing three solutions, the molybdenum content and temperature of which are different. In carrying out the experiments furnishing the data for the graph, the strike solution in each instance contained 16 gms./liter of sodium hydroxide, 16.4 gms./liter of the chelating agent, Versene T, which will be further identified hereinafter, and 10 gms./liter of borax. The molybdenum content of the strike solution referred to as "full strength molybdenum" was 10 gm./liter (expressed as molybdic oxide) and the molybdenum content of the strike solution referred to as "half strength molybdenum" was 5 gm./liter (expressed as molybdic oxide). The temperatures given are, of course, the temperatures of the strike solutions.

Fig. 4 of the drawings illustrates graphically the effect of the alkalinity of the strike solution on the weight of molybdenum (expressed as Mo) present in a strike deposit on 6061 alloy by employing two strike solutions

which differ only in alkalinity. To obtain the data for the graph, a 6061 aluminum alloy article was immersed in each of the strike solutions for times of 2, 4, 6 and 8 minutes. One of the solutions contained 1.65% by weight of free alkali (as NaOH) and the other contained 2.00% by weight free alkali (as NaOH). Both of the solutions contained 10 gms./liter of MoO_3, 16.4 gms./liter of Versene T and 10 gms./liter of borax. In each of the tests conducted, the strike solution was maintained at a temperature of 100° F.

Thus it is seen that a desired molybdenum content of the strike deposit can be obtained by balancing over a wide area the factors of solution temperature, time of contact, alkalinity, and molybdic or tungstic oxide concentration in the strike solution. The individual values decided upon will be dictated in large measure by the economics of the particular operation being carried out.

In general, however, it may be stated that it has been found that the objects of this invention can be accomplished with as little as 0.2 gm. of molybdic oxide per liter of strike solution and as much as 20.0 gm. per liter. The corresponding amounts of tungstic oxide are 0.34 to 34 gm. per liter, the tungstic oxide being used in slightly greater amount because of the greater atomic weight of tungsten. These figures represent a variation of 100 to 1 in molybdenum or tungsten content of the strike solution, but it has been found that such variations result in a corresponding variation of only about 3.33 to 1 in the amount of molybdenum or tungsten present in the resulting strike deposit. This indicates that there is little advantage to be gained in using the higher amounts of molybdic or tungstic oxide, but there should always be sufficient of at least one of these materials present that its exhaustion from the solution during normal use does not cause its concentration in the solution to drop below a safe level.

The chelating agent is an essential ingredient of the strike solution, and while various chelating agents may be employed, that selected should qualify in two important respects. First of all, the chelating agent should be effective at the high pH of the strike solution, and, secondly, it should have a broad spectrum at such a pH, i.e. it should have the ability to chelate a wide variety of metal ions.

The chelating agents manufactured by the Dow Chemical Company of Midland, Mich., and belonging to the general class of aminocarboxylic acids and their sodium salts have all been found effective in some degree for use in the strike solution, the acids existing therein, of course, as an alkali metal salt. These chelating agents have been divided into groups referred to as "Versene," "Versenol," and "Iron Specialty" chelating agents. The "Versene" series of chelating agents usually have as their base the salts of ethylenediaminetetraacetic acid, although the salts of diethylenetriaminepentaacetic acid may replace the corresponding salt of ethylenediaminetetraacetic acid.

The "Versenol" series of chelating agents usually have as their base the tri-alkali metal salt of N-hydroxyethylethylenediaminetriacetic acid, but this may be replaced if desired by the alkali metal salt of N-hydroxyethyldiethylenetriaminetetraacetic acid.

Chelating agents of the "Iron Specialty" series contain in addition to an aminocarboxylic acid, a compound identified as "Versene Fe–3 Specific," which designation refers to the monosodium salt of N,N-di(2-hydroxyethyl)-glycine.

We have found that the chelating agent "Versene T," one of the "Iron Specialty" series, supplied as a 54% liquid by the Dow Chemical Company, because of its effectiveness at high pH ranges is particularly advantageous for inclusion in the strike solution for use in the present invention. Versene T is identified by the manufacturer as being a concentrated, clear, light, straw-colored, aqueous solution, completely soluble in water—

sp. gr. (25/25° C.), 1.19; pH (1% aqueous solution), 12.0.

We have also obtained satisfactory results with a mixture of triethanolamine and "Versene 100." The "Versene 100" is described by the Dow Chemical Company as the tetrasodium salt of ethylenediaminetetraacetic acid. It is an effective chelating agent for the divalent metals in alkaline solutions. Triethanolamine is particularly effective in chelating iron and aluminum in alkaline solutions. We have found that mixtures of the two, over a wide range of proportions, are satisfactory. For example, we find that a mixture of 13.3 lbs. of Versene 100 and 3.7 lbs. of triethanolamine to be satisfactory and economical.

We have also found that another class of chelating agents can be employed—the polyhydroxy carboxylic ("sugar") acids and their salts. For example, we have used sodium gluconate, sodium glucoheptonate, sodium citrate and tartaric acid. The sodium gluconate and glucoheptonate are particularly effective in chelating aluminum and are economical to employ. Care must be exercised to assure complete removal by rinsing for any residue causes blackening of the enamel during firing because of reduction by the carbonaceous residue of incompletely rinsed polyhydroxy acid.

In addition to its role in preventing formation of objectionable compounds of magnesium at the alloy surface as pointed out earlier, the chelating agent serves the very important function of sustaining the aggressiveness of the strike solution toward aluminum. In the absence of the chelating agent, the vigor of the attack of the solution upon the surface of the alloy article slows progressively with the result that after several days very little effectiveness remains, even though the solution is not depleted through use. On the other hand, with the chelating agent present, the solution is effective for months until it finally becomes so charged with alkali aluminate from the action of the solution on the alloy surface that it must finally be discarded and a fresh solution prepared.

Moreover, if it were not for the chelating agent, the alkali aluminate, which is soon present in the strike solution, would combine with magnesium and other ions to throw down insoluble aluminates. This is prevented when the chelating agent complexes the magnesium or other metal as quickly as it goes into solution.

An additional function of the chelating agent is to keep the alloy surface clean and vulnerable to the action of the alkaline strike solution.

The amount of chelating agent in the strike solution is not at all critical, and it is practically an impossibility to set forth an effective range for this essential ingredient of the strike solution. It has been found that as little as 0.64 gm./liter of the chelating agent Versene T is an effective concentration, but it is preferred that at least 16.8 gm./liter be present. A great excess over this amount may be present without destroying the effectiveness of the chelating agent, but it is obvious that for economic reasons it would be foolish to add the chelating agent in amounts greater than that which provide maximum effectiveness in the operation of the process. Furthermore, we have noticed that large excesses over the amounts required create some problem in removal by rinsing.

As stated earlier, borax is not an essential ingredient of the strike solution and it is included because it contributes to free rinsing of the article after treatment. If this material is added to the strike solution, the amount which should be present is not at all critical. It has been found that from 2 gm. to 10 gm. per liter of solution are quite effective for the intended purpose.

Various methods may be used to contact the clean aluminum alloy surface with the strike solution. Immersion is preferred and for this purpose the strike solution may be contained in ordinary steel tanks. Other methods for contacting the surface to be enameled may, of course, be employed such as, for example, spraying.

It has already been pointed out, particularly with respect to the graphs of Figs. 3 and 4, that the factors of strike solution temperature and time of contact of the solution with the alloy surface to be enameled can be varied widely. The treatment with the strike solution may be carried out at ambient temperature but, as clearly shown by the graph, the operation is considerably accelerated by employing elevated temperatures, and it is prefered that the solution be heated if a source of heat is available at a sufficiently low cost. This assures that constant solution temperatures can be maintained even though ambient temperatures vary. Temperatures as high as 55° C. may be used without adversely affecting the character of the deposit formed on the alloy surface.

When a strike solution having relatively high molybdic or tungstic oxide content is employed at elevated temperatures, it has been found that contact times of only a few seconds are sufficient to produce a strike deposit having a molybdenum or tungsten content within the effective range. This also is shown by the graph of Fig. 3, and seldom, if ever, need the solution contact the alloy surface for more than five minutes.

After treatment of the aluminum alloy article with the strike solution for the desired time, the reaction is immediately stopped by rinsing the article with water. This may be accomplished either by spraying or by immersion. Preferably, there will be employed a cold water rinse followed by a hot water rinse, with the treated article being dried by forced warm air.

The strike solution of the present invention may be used over and over for long periods of time, even for many months. The caustic is depleted fairly rapidly during its attack on the alloy surface with the formation of sodium aluminate and evolution of hydrogen, and it must be periodically replaced. This is checked by titration, and the caustic is added as necessary to maintain the free alkali content of the solution within the necessary range. It is the build-up of sodium aluminate in the solution which finally dictates when the treating solution must be discarded and replaced by a fresh one.

The strike deposit is a thin amorphous film consisting of aluminum as well as the other metals present in the aluminum alloy, plus molybdenum or tungsten. They are probably present in the form of their oxides. The amount of this film depends upon the temperature and alkalinity of the strike solution and upon the period of immersion. For best results, the total weight per square foot of surface is kept between 10 and 50 milligrams. Although the total quantity of the strike deposit is influenced by the factors listed above, they do not appreciably affect its composition.

The only metal acquired from the solution is molybdenum (or tungsten), the rest are residues from the aluminum alloy and are present in the proportions found in that alloy, minus a major amount of aluminum and a minor amount of silicon that are lost into the solution.

The molybdic or tungstic oxide content of the strike solution is also obviously depleted in use, but this is at such a slow rate that it may be compensated for at the time the solution is initially prepared by employing an excess of molybdic or tungstic oxide over that which is required to insure an adequate molybdenum or tungsten content in the strike deposit. There is apparently no depletion of the chelating agent during the use of the strike solution, other than that lost by "drag-out."

As stated earlier, the surface of the aluminum alloy article should be clean prior to its being contacted with the strike solution, and this may be accomplished by conventional treatment. The choice of cleaning procedure will depend upon the nature of the shapes to be cleaned and the type of soil to be removed, etc. On work that is not heavily soiled nor corroded, a recommended procedure is to first remove the organic matter

in a so-called non-etch alkaline cleaning bath such as Ridolene No. 53 (American Chemical Paint Company) or the Diversey Corporation's No. 808, employing the concentration and temperature recommended by the manufacturer. This should be followed by a clear water rinse.

The work should then be immersed either in a cold deoxidizing bath such as Diversey's No. 514 or Oakite 34 or preferably in a hot bath containing sulfuric acid and chromic acid, as is described in U.S. Patent No. 2,719,796. After six minutes' immersion in such a bath, followed by adequate rinsing in clear water, the work is ready for immersion in the strike solution. In some instances, such as badly corroded stock and particularly in the case of extrusions, it may be desirable to follow the deoxidizing bath with an immersion in an etching bath such as Diversey's Aluminux. This should be made up and used according to the manufacturer's instructions. The work should be etched no more than is required for satisfactory results. The etch bath should be followed by a clear water rinse and then the work should be returned to the deoxidizing bath and thence on through the cycle.

Immediately after treatment of the alloy surface with the strike solution, it is ready for the enameling operation, itself, although this may be delayed, if desired. For enameling, there may be used any of the vitreous enamel frits ordinarily employed for the enameling of aluminum articles and available on the open market. These compositions ordinarily have as their foundation a lead borosilicate glass, and have maturing temperatures in the neighborhood of 1000° F., which is below the temperature at which the aluminum alloys soften and sag. U.S. Patent No. 2,467,114 is exemplary of a type of frit composition which may be used in the preparation of the slip that is to be used to enamel the pretreated articles of the present invention.

The frit compositions are converted into the enamel slip by grinding (usually in a ball mill) into a water suspension, together with the appropriate mill additions, colors, opacificers, etc. The slips so formed will ordinarily have a pH in the neighborhood of 10.7 to 11.0 but it is not unusual that a particular slip will have a pH as high as 12.5 to 13.0. This can result from grinding an excessively long time or by employing too high a ratio of water to frit, or by allowing the mill to heat up during grinding.

An excessively alkaline slip usually corrodes the aluminum alloy surface to which it is applied, particularly if it dries slowly. The result is severe "tearing" of the enamel, "gassing," and lack of adhesion to the alloy. This probably results from the hydrogen released by the corrosion and from the presence on the alloy surface of corrosion products that are not readily soluble in the enamel.

The addition of potassium dichromate to the slip has occasionally been resorted to in the past to reduce this corrosive action of an excessively alkaline slip. It has the disadvantage of coloring the resulting enamel and of reducing its adhesion to the alloy. We have discovered that phosphomolybdic acid is highly effective in reducing the corrosion of an excessively alkaline slip. Its use does not color the enamel, and it not only is highly effective as a corrosion inhibitor, but also has extraordinary capacity to neutralize alkali. Best results have been obtained by determining the total alkalinity of the slip in terms of weight of sodium hydroxide per unit weight of the slip. Crude phosphomolybdic acid is then milled or vigorously stirred into the slip to the amount of 1 unit weight of phosphomolybdic acid to approximately 4.5 unit weights of sodium hydroxide. An adjustment of viscosity is usually required.

Moreover, the pretreatment of an aluminum alloy surface in accordance with the present invention has been found, of itself, to greatly minimize the problems arising from the employment of an excessively alkaline slip. The surface of the alloy is provided with a protective film that enables it to tolerate a slip whose alkalinity would cause trouble if applied to a cleaned but unprotected aluminum alloy surface.

The porcelain enamel slips intended for aluminum and for other purposes requiring low-firing conditions have very poor storage properties. On standing for a matter of a week or so and occasionally only a few days, they become lumpy and finally harden into a solid mass. This represents a considerable loss.

We have discovered that the addition of a small amount of copper, in the neighborhood of .02 to .03% by weight of the frit employed, to the mill formulation before grinding will extend its storage life to at least 11 months. For example, two gallon ball mills of slip were prepared simultaneously. Each employed the same standard slip formulation. To one was added 0.25 gm. of cupreous powder. The slip without the copper hardened and could not be used after 2½ to 3 weeks. The one containing the copper could, after eleven months, be easily stirred with a spoon to a sprayable consistency, and produced a satisfactory enamel. The only effect on color was to alter pure white to pale cream. This was obscured in colors of appreciable depth.

The copper may be added as the free metal, and it has been found most convenient to add it as cupreous powder which may be in the form disclosed by Hubbell U.S. Patent No. 2,420,540.

We have also discovered that these enamel slips containing copper will occasionally adhere to adequately cleaned 6XXX alloy surfaces without pretreatment. X-ray studies have indicated the possible explanation. Magnesium disilicide will decompose in water, particularly at high pH, and the magnesium will then hydrate. The presence of copper in the amounts indicated prevents this.

The enamel slip may be applied by any suitable means to provide a layer of the desired thickness and fired at the indicated temperature in the neighborhood of 1000° F. immediately thereafter. On the other hand, if it is convenient for efficient plant operation, the enamel slip may be allowed to dry slowly before firing, without any of the undesirable results which would certainly have occurred if the article surface had not been pretreated with the strike solution.

Because of the increased adhesion brought about by the pretreatment of this invention, the slip compositions may include suitable mineral colors and opacifiers to provide a so-called "cover coat" and be applied directly to the pretreated surface of the alloy without the necessity of first applying a "grip coat" as has often been necessary with the prior art processes. A "grip coat" may, however, be used if desired.

As illustrative of, but not limiting the present invention, reference may be had to the following examples:

EXAMPLE I

A solution was prepared which had the following composition:

	G.
Sodium hydroxide	16.0
Molybdic oxide	0.2
Versene T	16.8
Borax	10.0

Water, sufficient to make 1 liter.

The solution was heated to 38° C. and three 4" x 6" panels of previously cleaned 6061 aluminum alloy were immersed in the solution for four minutes, rinsed in cold water, then in water at 54° C. and dried.

To a surface of two of the panels so treated there was applied a moist slip prepared from conventional vitreous enamel frit used for the enameling of aluminum. The slip was dried and the panels were fired at a temperature of approximately 530° C. There was formed on

these two panels a tightly adherent vitreous coating which showed no deterioration when immersed for 96 hours in 5% ammonium chloride solution (accelerated spall test).

The strike deposit was stripped from the panel which was not enameled, and on analysis, it was found that the molybdenum content (expressed as Mo) of the strike deposit was 1.44 mg./sq. ft. of treated surface.

EXAMPLE II

A solution was prepared which had the following composition:

	G.
Sodium hydroxide	16.0
Molybdic oxide	2.0
Versene T	16.8
Borox	10.0

Water, sufficient to make 1 liter.

Three 4" x 6" panels of previously cleaned 6061 aluminum alloy were treated as in Example I. The two panels which were enameled were found to have a tightly adherent vitreous coating which successfully passed the accelerated spall test. The panel which was not enameled was found to have a molybdenum content (expressed as Mo) in the strike deposit of 2.16 mg./sq. ft. of surface treated.

EXAMPLE III

A solution was prepared which had the following composition:

	G.
Sodium hydroxide	16.0
Molybdic oxide	20.0
Versene T	16.8
Borax	10.0

Water, sufficient to make 1 liter.

Three 4" x 6" panels of previously cleaned 6061 aluminum alloy were treated as in Example I. The two panels which were enameled were found to have a tightly adherent vitreous coating which successfully passed the accelerated spall test. The panel which was not enameled was found to have a molybdenum content (expressed as Mo) in the strike deposit of 9.36 mg./sq. ft. of surface treated.

EXAMPLE IV

A solution was prepared which had the following composition:

	G.
Sodium hydroxide	16.0
Tungstic oxide	0.34
Versene T	16.8
Borax	10.0

Water, sufficient to make 1 liter.

Three 4" x 6" panels of previously cleaned 6061 aluminum alloy were treated as in Example I. The two panels which were enameled were found to have a tightly adherent vitreous coating which successfully passed the accelerated spall test. The panel which was not enameled was found to have a tungsten content (expressed as W) in the strike deposit of 2.30 mg./sq. ft. of surface treated.

EXAMPLE V

A solution was prepared which had the following composition:

	G.
Sodium hydroxide	16.0
Tungstic oxide	3.4
Versene T	16.8
Borax	10.0

Water, sufficient to make 1 liter.

Three 4" x 6" panels of previously cleaned 6061 aluminum alloy were treated as in Example I. The two panels which were enameled were found to have a tightly adherent vitreous coating which successfully passed the accelerated spall test. The panel which was not enameled was found to have a tungsten content (expressed as W) in the strike deposit of 5.05 mg./sq. ft. of surface treated.

EXAMPLE VI

A solution was prepared which had the following composition:

	G.
Sodium hydroxide	16.0
Tungstic oxide	34.0
Versene T	16.8
Borax	10.0

Water, sufficient to make 1 liter.

Three 4" x 6" panels of previously cleaned 6061 aluminum alloy were treated as in Example I. The two panels which were enameled were found to have a tightly adherent vitreous coating which successfully passed the accelerated spall test. The panel which was not enameled was found to have a tungsten content (expressed as W) in the strike deposit of 7.65 mg./sq. ft. of surface treated.

Thus, it is seen that by pretreatment of an aluminum alloy of the magnesium-silicon series as described herein, there is produced the product diagrammatically shown in Fig. 1 of the drawings. There is provided on the surface of the alloy base 1, by contact with the strike solution, a deposit designated by the numeral 2. This deposit is extremely thin, but it permits the article to be successfully enameled by procedures which otherwise would fail completely.

The final enameled article is shown diagrammatically in Fig. 2, in which the numeral 1 again designates the aluminum alloy base, and the numeral 3 is the vitreous layer or coating which results after firing of the enamel slip. In the final article, the strike deposit has disappeared by diffusing into the base alloy and dissolving into the vitreous coating, or at least it has lost its separate identity. The vitreous coating is permanently and tightly adhered to the base alloy and remains so adhered indefinitely, even under the most adverse weather conditions.

It will be understood, of course, that in the present specifications and claims, reference to an aluminum alloy or an aluminum alloy article includes a structure in which a base metal is coated with an aluminum alloy, such as, for example, the well-known aluminized steel.

The present application is a continuation-in-part of our prior application S.N. 542,238, filed October 24, 1955, which is in turn a countinuation-in-part of our earlier application S.N. 500,988, filed April 12, 1955, now abandoned.

Having thus described the invention, what is claimed is:

1. The process of enameling an article composed of an aluminum alloy of the magnesium-silicon series, comprising: contacting the surface of said article with an aqueous solution of an alkali metal hydroxide, a metal oxide selected from the group consisting of molybdic oxide and tungstic oxide, and a broad-spectrum chelating agent effective at high pH, said solution having a free alkali content of 0.8 to 2.5 percent by weight expressed as alkali metal hydroxide; terminating the contact of said surface with said solution upon deposition on said surface of said article of from 1 mg. to 12 mg. per sq. ft., based on the weight of the element, of a compound selected from the group consisting of molybdenum and tungsten compounds; applying to said surface a vitreous enamel slip having a maturing temperature below the softening temperature of said alloy; and firing said article to form a tightly and permanently adherent vitreous coating thereon.

2. The process of claim 1 in which said alloy is "6061."

3. The process of claim 1 in which said alloy is "6063."

4. The process of claim 1 in which said chelating agent is a polyhydroxycarboxylic acid.

5. The process of claim 1 in which said slip contains a small amount of a finely divided cupreous powder.

6. The process of claim 1 in which said slip contains a minor amount of phosphomolybdic acid.

7. The product prepared by the process of claim 1.

8. The process of claim 1 in which said chelating agent comprises an aminocarboxylic acid.

9. The process of claim 8 in which said chelating agent comprises a mixture of ethylenediaminetetraacetic acid and triethanolamine.

10. The process of claim 8 in which said chelating agent comprises a mixture of ethylenediaminetetraacetic acid and N,N-di(2-hydroxyethyl) glycine.

11. The process of claim 10 in which said contact of said surface with said solution is terminated upon deposition on said surface of from 2 mg. to 6 mg. per sq. ft. of said compound.

12. The process of claim 11 in which said metal oxide is molybdic oxide.

13. The process of enameling a "6061" aluminum alloy article, comprising: contacting the surface of said article with an aqueous solution of sodium hydroxide containing free alkali within the range of from 0.8 to 2.5% by weight, said solution also containing molybdic oxide and a chelating agent comprising a mixture of ethylenediaminetetraacetic acid and N,N-di(2-hydroxyethyl) glycine; terminating the contact of said surface with said solution upon deposition on said surface of said article of 2 mg. to 6 mg. per sq. ft., based on the weight of the element, of a molybdenum compound; applying to said surface a vitreous enamel slip having a maturing temperature below the softening temperature of said alloy; and firing said article to form a tightly and permanently adherent vitreous coating thereon.

14. The process of claim 13 in which said solution contains from 2 gm. to 10 gm. per liter of borax.

15. The process of pretreating the surface of an article composed of an aluminum alloy of the magnesium-silicon series to prepare it for coating with a vitreous enamel, comprising: contacting the surface of said article with an aqueous solution of an alkali metal hydroxide, a metal oxide selected from the group consisting of molybdic oxide and tungstic oxide, and a broad-spectrum chelating agent effective at high pH, said solution having a free alkali content of 0.8 to 2.5 percent by weight expressed as alkali metal hydroxide; and terminating the contact of said surface with said solution upon deposition on said

surface of said article of from 1 mg. to 12 mg. per sq. ft., based on the weight of the element, of a compound selected from the group consisting of molybdenum and tungsten compounds.

16. The process of claim 15 in which said alloy is "6061."

17. The process of claim 15 in which said alloy is "6063."

18. The process of claim 15 in which said chelating agent is a polyhydroxycarboxylic acid.

19. The product prepared by the process of claim 15.

20. The process of claim 15 in which said chelating agent comprises an aminocarboxylic acid.

21. The process of claim 20 in which said chelating agent is a mixture of ethylenediaminetetraacetic acid and triethanolamine.

22. The process of claim 20 in which said chelating agent comprises a mixture of ethylenediaminetetraacetic acid and N,N-(2-hydroxyethyl) glycine.

23. The process of claim 22 in which said contact of said surface with said solution is terminated upon deposition on said surface of from 2 mg. to 6 mg. per sq. ft. of said compound.

24. The process of claim 23 in which said metal oxide is molybdic oxide.

25. The process for pretreating the surface of a "6061" aluminum alloy article to prepare it for coating with a vitreous enamel, comprising: contacting the surface of said article with an aqueous solution of sodium hydroxide containing free alkali within the range of from 0.8 to 2.5% by weight, said solution also containing molybdic oxide and a chelating agent comprising a mixture of ethylenediaminetetraacetic acid and N,N-di(2-hydroxyethyl) glycine; and terminating the contact of said surface with said solution upon deposition on said surface of said article of 2 mg. to 6 mg. per sq. ft., based on the weight of the element, of a molybdenum compound.

26. The process of claim 25 in which said solution contains from 2 gm. to 10 gm. per liter of borax.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,932,584

April 12, 1960

Dean S. Hubbell et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 11, for "ammonum" read -- ammonium --; column 4, line 17, heading to TABLE II, after the italicized word "molybdenum" insert an italicized -- strike solution --; column 11, line 17, EXAMPLE II, for "Borox" read -- Borax --.

Signed and sealed this 15th day of November 1960.

(SEAL)

Attest:

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