ALUMINUM COATING PROCESSES AND COMPOSITIONS

Alvin R. Stetson, San Diego, Calif., assignor to Solar Aircraft Company, San Diego, Calif., a corporation of California

No Drawing. Application February 20, 1957
Serial No. 641,245
41 Claims. (Cl. 117—63)

This invention relates to methods and compositions for obtaining the deposition of a protective aluminum or aluminum alloy layer on articles of ferrous materials, stainless steels, and super alloys.

This application is a continuation-in-part of my earlier application Serial No. 430,455, filed May 17, 1954, for “Aluminum Coating Processes,” and now abandoned.

It is well known in the art that aluminum, when applied to ferrous alloys and other metallic alloys, exhibits certain rendering properties being particularly adapted to protecting the basis metal from oxidation for long periods of time at temperatures up to and exceeding 2000° F.

There are many examples of aluminum coating and plating in the prior art. Included among these are processes in which the part to be coated is first covered, as by spraying or dipping, with a suspension of aluminum powder in a liquid vehicle, and then is fired to cause the aluminum to diffuse to form a solid solution and intermetallics with the basis metal of the coated part. A typical process of this type is disclosed in United States Patent No. 1,817,888 to Lowe. Processes in which the part is hot dipped in a bath of molten aluminum to provide an aluminum coating diffusion bonded to the basis metal have also been developed. One process of this general type is disclosed in United States Patent No. 2,569,097 to Grange.

Metal powder suspension and hot dip processes have been known for many years and recognized as having many advantages over other coating processes, such as electroplating and molten metal spray, for example. Nevertheless, they have not enjoyed wide commercial success because the results obtainable by their use have not in the past been consistently reproducible. Also, the coatings produced by such prior processes were not imperforate, uniform, or controllable in thickness frequently were not everywhere securely bonded to the basis metal. The hot dip processes tend to dissolve the basis metal in the aluminum bath and the coating thickness are limited. Furthermore, such hot dip processes are not adapted to coating articles of complex form or in which maintenance and coverage of sharp corners, and minimization of distortion are important. Also, certain of these prior processes employ fluxing agents which remain embedded as particles of slag in the finished coating, thus weakening the coating mechanically and rendering it susceptible to formation of perforations or pinholes on subsequent removal of the slag inclusions.

I have found that the particular fluxing agent employed in metal powder suspension (and hot dip processes) is a critical factor in the production of imperforate coatings of uniform thickness by those processes. For producing imperforate coatings of requisite uniformity and strength, the fluxing action must provide thorough cleansing of all oxides and other impurities from the surface of the basis metal, in order that the molten coating metal may evenly cover and uniformly wet and alloy with the basis metal. The flux must also be easily washed or otherwise removed from the finished coating, and not be embedded therein so as to cause discontinuities in the coating when removed. In the case of aluminum powder suspension processes in particular, the flux must also act to remove any oxides formed or present on the particles of aluminum powder and to form a continuous flux cover sealing the coating and basis metals from the atmosphere, to prevent further oxidation of these metals during the firing step. It is the purpose of this invention to provide improved processes for covering metallic surfaces with protective metal coatings in which the surfaces to be coated are wetted with molten aluminum in the presence of a flux composition which has a fluxing action satisfying the requirements outlined above and which is adapted for use in my aluminumizing process including powdered aluminum suspensions. The flux compositions herein disclosed, however, are also excellent for use with molten metal coating processes.

Therefore, a primary object of my present invention is to provide novel methods of developing a highly protective diffused aluminum or aluminum alloy coating of controllable thickness on ferrous and other metallic alloys, including the so-called super alloys.

It is also a major object of this invention to provide novel flux compositions capable of use in aluminumizing processes and particularly my new metal powder suspension processes.

Yet another object is the provision of a series of novel slips particularly useful in carrying out my aluminum powder coating process.

It is also an object to provide novel aluminumizing compositions including as auxiliary ingredients agents for controlling fluidity and flow-out of the essential ingredients, in order that aluminum coatings of predetermined thickness and superior protective ability may be obtained.

It is still another object of the present invention to provide new improved aluminum coating processes and a novel coating slip composition therefor using methanol as a vehicle, thereby obtaining unexpected advantages in the coating processes with improved coating results.

It is another object of this invention to provide a new powder suspension coating process utilizing an inert atmosphere in such manner as to obtain improved aluminum coatings, especially for coating parts of large cross section or parts made of the so-called super alloys.

It is still a further object of this invention to provide novel aluminum coating processes and new fluxes therefor which are water soluble, whereby the flux is removable from the coated article by water wash or leaching at low cost on a practical production basis and deleterious effects on the coated article during flux removal are avoided.

Another object is the provision of novel aluminumizing processes which are extremely useful in repairing and correcting the aluminum coatings on parts on which said coatings have been damaged by forming, welding, or finishing procedures subsequent to initial coating, regardless of the method used to obtain the initial coat.

Still another object is the provision of processes by which may be obtained smooth aluminum coatings characterized by uniform thickness over all areas of complex parts involving louvers, weld seams, sharp corners that must be maintained, joints, and other like complexities.

Another object is to provide quicker, less expensive,
and simpler methods of aluminizing steel and other alloys, which may be practiced with facilities generally considered standard items in any porcelain enameling plant.

Further objects and advantages will become apparent as the description proceeds in connection with the appended claims.

In carrying out my improved aluminizing process, the metallic surface to be aluminized is wetted with molten aluminum in the presence of one of the fluxing agents described herein. This is accomplished by applying to the surface of the basis metal article, by spraying or dipping or the like, a slip composed of a suspension of flux and aluminum powder in a liquid vehicle, with or without flow control agents, and heating the article thus coated to a temperature in excess of the melting point of aluminum in air, or preferably in an inert atmosphere such as nitrogen. During the heating or firing cycle, the aluminum becomes molten and evenly covers and uniformly wets and to some degree alloys with the basis metal, producing a superior coating of two phases: (1) an interphase of diffused aluminum, and (2) a surface layer of aluminum covered with flux. The flux is subsequently removed by such means as hot water wash or leaching.

A properly controlled heat treatment may subsequently be used to improve the oxidation and corrosion resistance of the protective layer by causing further diffusion of the aluminum or aluminum alloy into the basis metal as hereinafter amplified. Excellent results are obtained, however, without such diffusion treatment, and the use of a subsequent diffusion cycle is generally applicable to the stainless steels and super alloys to develop an erosion resistance as well as oxidation and corrosion resistance.

In my aluminum powder suspension process, a first consideration is the provision of a slip comprising essentially aluminum or aluminum alloy powder and a chloride base flux carried in suspension in a liquid vehicle. Auxiliary components of the slip are a suspending agent and a binder. Small amounts of a refractory oxide, iron, nickel or a mixture thereof may also be included in the slip for purposes which will be described hereinafter.

Table I shows the general constituency of slips according to my invention:

<table>
<thead>
<tr>
<th>TABLE I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingredient</td>
</tr>
<tr>
<td>Aluminum Powder</td>
</tr>
<tr>
<td>Flux</td>
</tr>
<tr>
<td>Liquid Vehicle</td>
</tr>
<tr>
<td>Binder</td>
</tr>
<tr>
<td>Refractory Oxide</td>
</tr>
<tr>
<td>Iron and/or Nickel (aggregate)</td>
</tr>
</tbody>
</table>

Of great importance is the fact that the aluminum powder may vary considerably in both chemical composition and physical properties with no deleterious effect on the final protective coating. In general pure aluminum or silicon-aluminum alloys are preferred since these exhibit the most satisfactory resistance to corrosion and oxidation. I do not, however, wish to limit the scope of this invention to these two aluminum materials, since other aluminum alloys containing substantial copper, magnesium, manganese, and other metals, have proved useful for providing highly satisfactory protective coatings.

Although a grain size of minus 100 mesh plus 400 mesh is preferred when standard dip and spray techniques are used, in general any grain size is useful in my process. The size used is governed by the requirements of the specific application. Also, both atomized aluminum powder and flake aluminum can be successfully used in my process, although atomized powder is the preferred material.

The fluxing agent is a critical factor in the production of satisfactory coatings as pointed out above. My new improved fluxing agent is a chloride base flux consisting of a metal halide mixture the principal part by weight of which consists of chlorides of sodium and potassium and the balance of which consists essentially of lithium fluoride and cryolite. Examples of flux compositions I have found satisfactory are listed in Table II.

<table>
<thead>
<tr>
<th>TABLE II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingredient</td>
</tr>
<tr>
<td>KCl (potassium chloride)</td>
</tr>
<tr>
<td>NaCl (sodium chloride)</td>
</tr>
<tr>
<td>NaF (lithium fluoride)</td>
</tr>
<tr>
<td>NaF.PF3 (cryolite)</td>
</tr>
<tr>
<td>AlF3 (aluminum fluoride)</td>
</tr>
</tbody>
</table>

Compositions 1 through 6 inclusive function satisfactorily on steels having less than about 15 points of carbon, and composition 7 functions satisfactorily on alloys of both low and high carbon content. Since compositions 1 through 6 are the more water soluble they are preferably used where applicable, because they can be readily removed by inexpensive non-deleterious water wash.

The melting point of the flux may be varied by varying the ratio of KCl to NaCl. For example, I find that when pure aluminum or such alloys as copper-aluminum and magnesium-aluminum are used as the coating ingredient, the ratio of KCl to NaCl should not be less than 1.12 and is preferably about 1.1. However, when a high silicon-aluminum alloy or a magnesium-aluminum alloy is utilized, it is preferred to lower the melting point of the flux by increasing the ratio of KCl to NaCl to approximately 1.3:1. Of course, the ratio may be varied to obtain the desired melting point for each alloy. In my experience, the most satisfactory flux composition has an aggregate chloride content of from 70% to 88% by weight of the total, the chlorides being present in a potassium chloride-sodium chloride ratio between 1.3:1 and 1:1.2.

The aggregate fluoride content is preferably 12% to 30% by weight of the total, with the lithium fluoride ranging from 3.5% to 20%, the cryolite from 8.5% to 20%, and aluminum fluoride from 0 to 20% of the total. I have found that this combination of lithium fluoride, cryolite, and aluminum fluoride is more satisfactory than any of the fluoride components singly. The fluorides, which are the active constituents of the flux, promote the wetting and flotation of the basis metal oxides (which will be iron oxides if the basis metal is ferrous) and the aluminum oxides.

The flux is formulated to clean the surface of the basis metal prior to the melting of the aluminum. Otherwise, agglomeration of the aluminum powder will prevent complete coverage of the work piece. The flux compositions of Table II provide this necessary cleaning action. Being the first constituent of the bisque to melt, the flux first wets and spreads on the surface of the basis metal free of the oxides existing or formed on the basis metal prior to the fusion of the flux. Further oxidation is prevented by the flux cover. Then, as the aluminum melts, the flux dissolves and washes away the aluminum oxide on the aluminum powder. When both basis metal and aluminum are free of oxide, the aluminum flows evenly over and wets the surface of the basis metal to form a diffused layer of aluminum in solid solution with the basis metal topped by a layer of pure aluminum or aluminum alloy. The fluorides, which are the active constituents of the flux, promote the dissolution, wetting and flotation of the basis metal oxides and the oxides of aluminum.

The liquid vehicle selected will vary with requirements of the specific application. Although I prefer to use an organic solvent such as, for example, as methyl alcohol, butyl Cellosolve or Stoddard solvent, I have achieved useful results with water as the slip vehicle. However, when water is utilized as the vehicle, it is essential to include in the slip an inhibitor agent for preventing hy-
hydrogen reaction and corrosion. Ammonium chromate has been found to be a satisfactory inhibitor. However, the coating cycle should be completed within 30 minutes when coating in water, or there will be a strong possibility of reaction with the finely divided aluminum powder and the water with possibly dangerous hydrogen generation. Any organic solvent, such as above noted is superior to water as a vehicle, especially in production where long life of the slip is essential, and the coating cycle frequently may not be completed within 30 minutes after the slip is made.

When water is the vehicle, sodium carboxethyl cellulose, sodium alginate and a number of alginic acid derivatives provide a satisfactory suspending agent. With organic solvent vehicles, ethyl cellulose, aluminum stearates, and aluminum octoates are good suspending agents. In either case, the suspension agent acts in part as a binder, providing a hard bisque when the slip is dried so that the article coated can be more readily handled. The binding action may be enhanced by addition of any of the coumarone-indene type resins.

Methyl alcohol (methanol) has proven to be an unexpectedly especially good agent for the alumizing processes of this invention. It is the only slip vehicle discovered to date which does not require an auxiliary binder to obtain a hard bisque that can be handled after drying. Crystallization on drying provides the necessary dry bisque strength for handling the parts. Hence, the use of methanol obviates the necessity of a bisque binder, such as coumarone-indene resins, which must be burned out in the firing cycle. Higher quality coatings can be obtained with a methanol vehicle for this reason.

I have found that the addition of small amounts (up to 5 parts by weight) of a finely divided refractory oxide such as alumina to the aluminum stearate will decrease the fluidity of the flux during the firing cycle, thereby inhibiting it from flowing away from the particles of aluminum and result in a superior cleaning action on the aluminum powder.

The thickness of the finished coating may readily be controlled to within one-thousandth of an inch by varying the amount of aluminum powder applied to each unit area of the surface being coated. This may be done either by varying the thickness of the layer of slip deposited on the surface or by varying the concentrate of aluminum powder in the slip. If, however, the aluminum powder is supplied in too great amount, as for the purpose of obtaining an extremely thick coating, there may tend to flow too freely about on the surface when melted during the firing cycle. This may cause the coating alloy to drip from the surface edges or accumulate at low points on the surface of the article, causing the finished coating to be non-uniform in thickness. I have found that this difficulty may be obviated in heavier coatings, and uniform thickness obtained, by adding small amounts up to 10 parts by weight of iron or nickel or a mixture of these metal powders to the slip. These additives increase the viscosity and limit flowout of the molten aluminum so that a thicker layer will remain in place on the surface during the firing cycle.

It has been found that a coating which adds 1 to 3 mils to the surface thickness will provide excellent oxidation protection. Low alloy steels are usually coated with 3 mils of aluminum, while the higher alloys of chromium and nickel and chrome-vanadium-nickel-chromium-iron, with other alloying elements, usually require only approximately 1 mil of aluminum. Low alloy parts coated to 3 mils thickness have been tested in air at furnace temperatures of 1500° F. for more than 100 hours with no measurable oxidation. The 15-8 stainless steels have been exposed 20 hours at 2400° F. with no change in the original thickness of the sample through oxidation. Other results with various metals and alloys have been equally satisfactory.

In Table III are listed seven slips I have found satisfactory, although it should be understood many variations may be made without departing from the spirit of the invention:

| Table III (Solids shown in grams, liquids in milliliters) |
|-----------------|-----------------|-----------------|-----------------|
| Ingredient      | 1   | 2   | 3   | 4   | 5   | 6   | 7   |
| Aluminum Powder | 33.2| 30  | 30  | 25  | 25  | 25  | 25  |
| Flux (NaOH)     | 65.2| 65  | 65  | 65  | 65  | 65  | 65  |
| Sodium Alginate | 2   | 0   | 0   | 1   | 0   | 0   | 1   |
| Starch          | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Ammonium Chromate (NH4O6O4) | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| Aluminum Stearate | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Aluminum Octoate | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| Iron and/or nickel (Al-grenate) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Methyl Alcohol | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

Any organic solvent that will not react with aluminum.

A preferred coating cycle, which may be varied to suit various specific applications without departing from the spirit of my invention, would be as follows:

The part to be aluminized may be degreased, then cleaned by such methods as light pickled or light sandblast. It should be understood that, where in many prior art processes, a heavy pickle and sandblast are required to develop a rough surface to improve adherence, I have found that my process will develop a superior bond equally well on a smooth surface, for example, a No. 4 finish stainless steel, which is classed as a mirror finish.

The absence of any need for roughening the surface of the parts preparatory to application of my coatings presents many advantages among which are the saving in time and cost of preparing the surface for coating, and the ability to coat thin sheet material such as metal foil and the like which cannot withstand the extensive treatment required for surface roughening. A further advantage is presented where a relatively thin coating is to be applied to a smooth surface. Since the surface need not be roughened prior to being coated, the coating may be made very thin without sacrifice of appearance due to the inability of such a coating to hide surface roughness.

After the part has been cleaned it is spray, brush, or dip coated with aluminizing slip and the slip dried, preferably, but not necessarily, in an oven. The part may then be fired to cause the flux and aluminum powder to melt and the aluminum to alloy with the basis metal. Firing should be just long enough to bring the part to heat and hold it approximately 5 minutes. The time at temperature is determined by the extent of diffusion desired. I have found, for example, that for many parts fabricated of .050-.078 sheet, the firing cycle is completed in from 5 to 10 minutes at a temperature range of 1220°-1500° F. The temperature is determined by the thickness of the article, the diffusion desired, and the need to melt the flux before excessive oxidation of the basis metal develops. Depending upon the article and complexities of design higher temperatures may be used. For coating of thin sheets a temperature range of 1300° F. to 1400° F. is preferred, and on thicker articles in general it is preferred to maintain temperatures below 1500° F. Where fast cooling is preferable, it is preferable on low alloy steels to fire below the transition points of the basis metal to minimize distortions. The best coating temperature in each specific application can be readily determined by test.

Following air cool, the flux residue may be removed in a hot water wash. A passivating treatment in dilute nitric acid may follow to produce a clean, white surface. It has been found advantageous to use an inert atmosphere in the firing of these aluminum coatings, especially for parts of large cross-section, which can be heated only slowly in the furnace. Such large parts may oxidize
excessively before the flux is molten, unless an inert atmosphere is used, and a heavy oxide will preclude a... 7

Subsequent heat treatment of the thus-coated article may be utilized to improve the oxidation and corrosion resistance of the protective coating layer by causing further diffusion of the aluminum or aluminum alloy into the basis metal. For the mild steels and other low alloys, this heat treatment may be carried out in a temperature range of 1500-1750° F. for about one hour; for the stainless steels and other high alloys, a temperature in the range of 1750-2150° F. is desirable if the time is limited to one hour. However, in either case, the temperature and time are related, and a lower temperature may be successfully employed if the time is extended.

To an extent, this further diffusion and adequate protection develop automatically when the protected part is subjected to service temperatures above 900° F. for an extended period of time. Excellent results are obtained, however, without diffusion, and the use of a diffusion cycle is generally applicable to the stainless steels and super alloys to develop an erosion resistance as well as the oxidation and corrosion resistance.

It has been found that removal of the oxidation product after diffusion, by a hydroblast or similar process using 220 mesh or finer grit, greatly improves the durability of the coating, especially if service is about 1500° F.

Following are two typical specific coating treatments A and B which are illustrative of my preferred powder-metal suspension coating process employing slips using methanol as the vehicle. Example A employs the preferred step of firing in an inert atmosphere, followed by diffusion treatment which gives better results with a super alloy like L-605.

A. Typical treatment of L-605 alloy

(1) Slip composition (No. 7 in Table III above).

100 parts by weight atomized aluminum powder, preferably Alcoa atomized aluminum Type 101.

100 parts by weight flux composition No. 7 in flux composition Table II, above.

4 parts by weight iron powder—325 mesh.

100 ml. methyl alcohol.

(2) Cycle of operation: vapor degrease, light sand-blast, apply slip by spraying approximately 7 mils biseque; fire in a nitrogen atmosphere 5 minutes at 1300° F.; rinse off flux in hot water; dip in hot nitric acid solution 140° F. for 1 minute to remove last traces of flux; diffuse in air 3 hours at 1850° F.; vapor blast with 220 grit sand for sat finish, if desired.

B. Typical treatment of mild steel screen

(1) Use same slip as outlined above.

(2) Cycle of operation: vapor degrease; pickle in 50 percent inhibited muriatic acid; neutralize in 1/4 percent sodium carbonate solution at 200° F.; apply slip by spraying to a uniform 8 mil biseque; fire in air at 1300° F. for 2 minutes; soak in hot water for 2 minutes to remove flux; air-water blast to remove last of flux.

It will be appreciated that these are only two examples of a great variety of possible applications, in accordance with the above-described inventions, and that they are included to show actual specific slip and cycle examples that give results superior to those obtainable with processes and compositions heretofore available.

Where it is necessary to do further work on a coated part, such as machining or welding, or where the coating has been damaged, I have found that the coating may be easily repaired by cleaning the affected area, brushing or spraying a layer of the slip over the area, and torch or furnace flame at a temperature high enough so that the part may be stripped of the coating and reprocessed, if desired.

My improved processes employing cold dipped or sprayed aluminum powder slips are particularly adapted to uses in which the part to be aluminumized is of complex geometry or very large size, and to uses in which the aluminum coating must be relatively thick or of very uniform thickness to meet close dimensional tolerances. As applied to such uses, these processes present many advantages over hot dip processes which are, in general, restricted to use with articles which are of such shape as to permit excess aluminum to be easily drained or shaken therefrom while the aluminum is still in the molten state.

I have found that the same fluxing agents described above with reference to my aluminum powder process may successfully be used in hot dip processes, however, and that these fluxing agents will yield outstanding results when so employed. In hot dip processes the flux is not mixed with aluminum powder, but is separately applied to the surface of the part being coated, and the surface thus fluxed is then immersed in a bath of molten aluminum. The flux may be applied to the surface of the part in the form of a slurry which is brushed or sprayed onto the surface of the part and permitted to dry thereon, or by melting a quantity of flux to form a liquid bath into which the part is dipped to coat its surface with flux.

Definition: The term "aluminum" used in the claims is defined as meaning a metal selected from the group consisting of aluminum and aluminum base alloys.

From the above disclosure, it will be seen that I have discovered and developed novel methods of forming highly protective aluminum base coatings on metallic surfaces, which methods have solved the many problems existing in the art. The invention may be embodied in other specific forms, without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced thereunder.

What is claimed and desired to be secured by United States Letters Patent is:

1. A method of applying a protective aluminum coating to the surface of a metallic article which comprises coating said article at room temperature with a mixture of aluminum in particle form and a water soluble flux, in an organic vehicle, said mixture containing a minimum of 25 percent by weight of said flux, said flux consisting essentially of from 70 to 88 percent by weight in the aggregate of chlorides of potassium and sodium present in a potassium chloride-sodium chloride ratio between 1:3:1 and 1:1:2, and from 30 to 12 percent by weight in the aggregate of lithium fluoride, cryolite and aluminum fluoride, with the lithium fluoride ranging from 3.5 to 20 percent, cryolite from 8.5 to 20 percent, and aluminum fluoride 0 to 20 percent of the total, heating said coated article to a temperature above the melting point of said flux and said aluminum powder to cause a layer of aluminum to wet and cover the article, and removing said water soluble flux by leaching in water.

2. The method of applying to a metallic article a protective metal coating which comprises coating the surface of the article with a composition including as essential ingredients thereof between 75 and 90 percent by weight of aluminum in particle form and 25 to 75 parts by weight of a fluxing agent consisting essentially of a metal halide mixture the principal part by weight of which consists of chlorides of sodium and potassium and the balance of which consists of alkali metal fluorides.
and aluminum fluoride, and heating said surface to a temperature at which the aluminum melts and wets and covers the article and alloys with said article.

3. A method of applying a protective metal coating to the surface of a metallic article as defined in claim 2, wherein said first-recited step comprises coating the surface of the article with a composition that also includes up to 5 parts by weight of alumina for decreasing the fluidity of said fluxing agent in said heating step.

4. A method of applying a protective aluminum coating as defined in claim 3, wherein the recited composition of aluminum, flux and alumina is suspended in a liquid vehicle forming a slip which is applied to said article surface.

5. The method of applying a relatively thick protective metal coating to the surface of a metallic article as defined in claim 2, wherein said first-recited step comprises coating the surface of the article with a composition that also includes up to 5 parts by weight in the aggregate of at least one metal selected from the group consisting of iron and nickel for inhibiting flow-out of said coating metal in said heating step.

6. A method of applying a protective aluminum coating as defined in claim 5, wherein said composition of aluminum, flux, and last-recited metal is suspended in a liquid vehicle forming a slip which is applied to said article surface.

7. The method of applying a protective metal coating to the surface of a metallic article as defined in claim 2, wherein said balance of the flux consists of lithium fluoride and at least one material from the group consisting of cryolite and aluminum fluoride.

8. The method of applying to the surface of a metallic article a protective metal coating of substantially uniform thickness as defined in claim 7, wherein said first-recited step comprises covering the surface of the article with a composition that includes a fluxing agent consisting essentially of from 70 to 88 percent by weight in the aggregate of chlorides of potassium and sodium present in a potassium chloride-sodium chloride ratio between 1.3:1 and 1.2:1 and from 30 to 12 percent by weight in the aggregate of lithium fluoride, cryolite and aluminum fluoride with the lithium fluoride ranging from 3.5 to 20 percent, the cryolite from 8.5 to 20 percent, and aluminum fluoride 0 to 20 percent of the total.

9. The method of claim 2 with the additional step of coating the protected metallic article to a subsequent heat treatment to further diffuse the protective aluminum layer into the coated article.

10. A method of coating mild steels and other low alloys as defined in claim 9, wherein the heat treatment consists of subjecting the metallic article to a temperature of from 1500–1750° F. for at least one hour.

11. A method of coating stainless steels and other high alloys as defined in claim 9, wherein the heat treatment consists of subjecting the metallic article to a temperature of from 1850–1950° F. for at least one hour.

12. A method of coating stainless steels and other high alloys as defined in claim 9, wherein the heat treatment consists of subjecting the article to a temperature of from 1750–2150° F. for approximately one hour.

13. The method of claim 9 together with the further step of using a hydroblast to remove the oxidation product resulting from said last-mentioned step.

14. The method of applying a protective aluminum coating as defined in claim 2, wherein said flux is water-soluble, further comprising the step of removing said water soluble flux by water wash.

15. The method of applying a protective coating as defined in claim 2, wherein said last-recited step is carried out in an inert atmosphere.

16. The method of applying a protective aluminum coating as defined in claim 2, wherein said last-recited step is performed in a nitrogen atmosphere.

17. A method of applying a protective aluminum coating as defined in claim 2, wherein the recited composition of aluminum and flux is suspended in a liquid vehicle forming a slip which is applied to said article to coat the surface thereof.

18. A method of applying a protective aluminum coating as defined in claim 17, wherein said liquid vehicle is methanol.

19. A method as defined in claim 17, wherein said liquid vehicle is water and the slip also includes a corrosion inhibiting agent and suspension agent.

20. A composition including as essential ingredients between 75 to 25 parts by weight of aluminum in particle form and 25 to 75 parts by weight of a fluxing agent consisting essentially of a metal halide mixture the principal part by weight of which consists of chlorides of sodium and potassium and the balance of which consists of lithium fluoride, and at least one material from the group consisting of cryolite and aluminum fluoride.

21. A composition as claimed in claim 20, wherein said fluxing agent consists essentially of from 70 to 88 percent by weight in the aggregate of chlorides of potassium and sodium present in a potassium chloride-sodium chloride ratio between 1.3:1 and 1.2:1 and from 30 to 12 percent by weight in the aggregate of lithium fluoride, aluminum fluoride, and cryolite, with the lithium fluoride ranging from 3.5 to 20 percent, the cryolite from 8.5 to 20 percent, and aluminum fluoride 0 to 20 percent of the total.

22. An anodizing slip comprising an aqueous suspension of the composition claimed in claim 20 and containing also a suspension agent and a corrosion inhibiting agent.

23. An anodizing slip as defined in claim 22, wherein said suspension agent consists of one or more materials selected from the group consisting of sodium carboxymethylcellulose, sodium alginate and algic acid derivatives, and said corrosion inhibiting agent is ammonium chromate.


25. An anodizing slip consisting essentially of the composition as defined in claim 24, further including a suspension agent.

26. An anodizing composition as defined in claim 20, having as a further constituent up to 5 parts by weight of alumina.

27. An anodizing composition as defined in claim 20, having as a further constituent up to 5 parts by weight of at least one metal selected from the group consisting of iron and nickel.

28. An anodizing slip consisting essentially of the composition as defined in claim 20, further including a suspension agent.

29. An anodizing slip as defined in claim 28, further comprising a binder agent.

30. An anodizing slip as defined in claim 29, wherein said binder agent is one of the coumarone-indene type resins.

31. An anodizing slip as defined in claim 28, wherein said suspension agent consists of one or more materials selected from a group consisting of ethyl cellulose, aluminum stearates and aluminum octoates.

32. An anodizing composition as defined in claim 20, having as a further constituent up to 10 parts by weight in the aggregate of at least one metal selected from the group consisting of iron and nickel.

33. An anodizing slip consisting essentially of a suspension of the composition defined in claim 20 in methanol.

34. An anodizing slip composition as defined in claim 33, having as a further constituent up to 10 parts by weight in the aggregate of at least one metal selected from the group consisting of iron and nickel.

35. An anodizing slip composition as defined in claim 34, wherein approximate proportions of said ingredients
are 100 parts aluminum powder, 1 part flux, 80 parts methanol and 4 parts iron, in parts by weight.

36. An aluminizing slip as defined in claim 35, further comprising a binder agent.

37. An aluminizing slip as defined in claim 36, wherein said binder agent is one of the coumarone-indene type resins.

38. A method of applying a protective aluminum coating to the surface of a metallic article which comprises coating said article with a mixture of aluminum in particle form and a water soluble metal halide flux suspended in a liquid vehicle, said mixture containing a minimum of 25% by weight of said flux, heating said article coated with said mixture to a temperature above the melting point of said flux and said aluminum to cause a layer of aluminum to wet and cover the article, and removing said water soluble flux by leaching in water.

39. A method of applying a protective aluminum coating to the surface of a metallic article as defined in claim 38, wherein said mixture of aluminum and flux includes between 25 to 75% by weight of said flux, and wherein said mixture is applied to said article at room temperature.

40. A method of applying a protective aluminum coating to the surface of a metallic article as defined in claim 39, wherein said article is coated with a mixture of said aluminum and flux in an organic vehicle.

41. A method of applying a protective aluminum coating to the surface of a metallic article which comprises coating said article at room temperature with a mixture of aluminum in particle form and a water soluble flux in a methanol vehicle, said mixture containing a minimum of 25% by weight of said flux, said flux consisting essentially of from 70 to 88 percent by weight in the aggregate of chlorides of potassium and sodium present in a potassium chloride-sodium chloride ratio between 1.3:1 and 1:1.2, and from 30 to 12 percent by weight in the aggregate of lithium fluoride, cryolite and aluminum fluoride, with the lithium fluoride ranging from 3.5 to 20 percent, cryolite from 8.5 to 20 percent, and aluminum fluoride 0 to 20 percent of the total, and heating said coated article in an inert atmosphere to a temperature of at least about 1220°F., and maintaining the coated article at said temperature a sufficient time to cause a layer of aluminum to wet and cover and alloy with said metal article.

References Cited in the field of this patent

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Inventor(s)</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,155,947</td>
<td>Van Allen</td>
<td>Oct. 5, 1915</td>
</tr>
<tr>
<td>1,565,496</td>
<td>Pfeil</td>
<td>Dec. 15, 1925</td>
</tr>
<tr>
<td>1,817,888</td>
<td>Lowe</td>
<td>Aug. 4, 1931</td>
</tr>
<tr>
<td>2,403,706</td>
<td>Bryant</td>
<td>July 9, 1946</td>
</tr>
<tr>
<td>2,466,971</td>
<td>Shawcross</td>
<td>Apr. 12, 1949</td>
</tr>
<tr>
<td>2,507,956</td>
<td>Bruno et al.</td>
<td>May 16, 1950</td>
</tr>
<tr>
<td>2,541,813</td>
<td>Fisch</td>
<td>Feb. 13, 1951</td>
</tr>
<tr>
<td>2,509,097</td>
<td>Grange et al.</td>
<td>Sept. 25, 1951</td>
</tr>
<tr>
<td>2,641,551</td>
<td>Smith et al.</td>
<td>June 9, 1953</td>
</tr>
<tr>
<td>2,671,737</td>
<td>Jominy et al.</td>
<td>Mar. 9, 1954</td>
</tr>
<tr>
<td>2,785,084</td>
<td>Lundin</td>
<td>Mar. 12, 1957</td>
</tr>
</tbody>
</table>