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METHOD OF ALUMINUM COATING

Original Filed Sept. 29, 1954

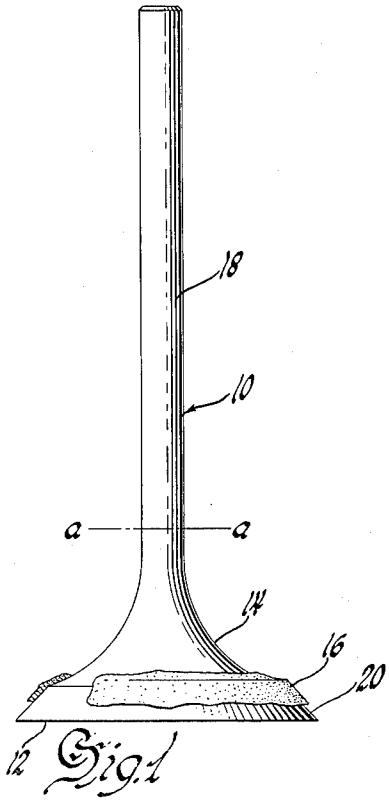


Fig. 1

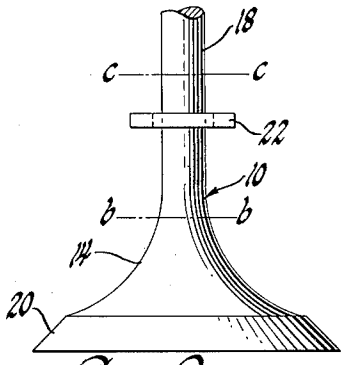


Fig. 2

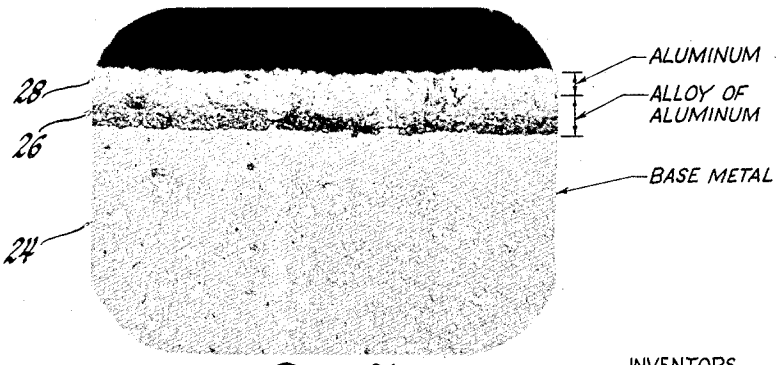


Fig. 3

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METHOD OF ALUMINUM COATING

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Original application Sept. 29, 1954, Ser. No. 459,093, now Patent No. 2,885,304, dated May 5, 1959. Divided and this application Mar. 16, 1959, Ser. No. 799,654

4 Claims. (Cl. 117—93)

This invention relates to metal coating operations and particularly to a method of providing a thin adherent coating of aluminum or aluminum base alloy on metals having a relatively low solubility in aluminum. The present process is especially adapted to aluminum coat ferrous base articles, such as poppet valves and the like.

This is a division of the copending application Serial No. 459,093 filed September 29, 1954, now Patent No. 2,885,304.

With the advent of high compression internal combustion engines and the more extensive use of leaded fuels in recent years, the valves in such engines have been subject to rapid oxidation and high temperature corrosion by the hot combustion gases. The gases which result from the burning of leaded gasolines are particularly detrimental and greatly shorten the life of exhaust valves of internal combustion engines. Consequently, exhaust valve failure frequently occurs either because of high temperature corrosion of the valve seating face or because of corrosion of the stem immediately adjacent the valve head. Severe corrosion of this stem can result in its necking down to a point where its stem will actually fracture.

To alleviate the aforementioned oxidation and corrosion problem and to considerably increase the lift of poppet valves, these valves may be coated with aluminum or aluminum base alloys. A process for coating valves with aluminum is disclosed in co-pending patent application S.N. 364,673 filed on June 29,1953, now abandoned, in the name of Dean K. Hanink. This process results in an aluminum coated valve having at or adjacent the surface of the base metal a thin layer of an alloy of aluminum and the base metal. This layer is provided at the valve seating face and also may be provided around the valve head and neck. For best results, the valve should have an extremely thin layer of aluminum or aluminum base alloy over the alloy layer.

The process described in the aforementioned co-pending patent application has proved to be very satisfactory. However, in order to more advantageously employ conveyor equipment in the coating of poppet valves and hence permit the use of a continuous coating process, the invention hereinafter described is preferably employed. Moreover, the present process not only may be carried on more rapidly but it also is relatively inexpensive since it reduces equipment requirements.

Of course, it will be understood that this process is also applicable for coating metal articles other than poppet valves, insofar as these articles have shapes and sizes which permit the utilization of this process. Examples of such articles are wire, woven metal fencing, rocker panels, tubing, bolts and nuts. The invention is hereinafter described in conjunction with valve coating operations primarily because the process is particularly effective for aluminum coating valves.

Accordingly, a principal object of this invention is to provide a simple, practical and inexpensive method of selectively aluminum coating metal articles without immersing them in molten aluminum. A further object of the present invention is to provide an aluminum coating on

metals having a relatively low solubility in aluminum, which coating is continuous and chemically alloyed to the article coated. A stull further object of the invention is to provide a rapid method of coating ferrous base poppet valves and the like with a thin, adherent layer of aluminum or aluminum base alloy having a controlled thickness which simplifies or eliminates the problem of removing excess coating metals.

The above and other objects are attained in accordance with the present invention by a process in which aluminum, either in paste or spray form or by means of a solid metallic member, is first applied to the article to be coated. The article is thereafter heated to melt the aluminum and provide a thin, continuous aluminum layer securely bonded to the base metal. This heating is best accomplished by immersing the article in a salt flux. Likewise, fluxing of the base metal surface may be provided by incorporating such a flux in the aforementioned paste. Generally, however, effective fluxing of the coated part and melting of the aluminum are preferably accomplished simultaneously.

When an aluminum base alloy is used as the coating material, this alloy should contain about 80% or more of aluminum. Unless otherwise indicated, therefore, the word "aluminum," as used herein, is intended to include not only pure aluminum and commercially pure aluminum, but also aluminum base alloys containing at least approximately 80% aluminum.

Other objects and advantages of this invention will more fully appear from the following detailed description of preferred embodiments of the invention, reference being made to the accompanying drawing, in which:

FIGURE 1 is a vertical elevational view, with parts broken away, of a poppet valve to be coated with aluminum in accordance with the preferred modification of the invention, the desired location of aluminum paste and areas of immersion being shown schematically;

FIGURE 2 is a fragmentary vertical elevational view of a poppet valve to be aluminum coated in accordance with another modification of the invention, schematically showing the depths of immersion, etc.; and

FIGURE 3 is a photomicrograph of a section through the valve seating face showing the ferrous base metal, the aluminum coating thereon, and the interjacent layer of an alloy of aluminum and the base metal.

In each instance the surfaces of the valve or other article to be coated are preferably cleaned prior to the aluminum coating and alloying operation. One satisfactory method is to clean these articles in a molten electrolytic caustic salt (such as the commercially available product called Kolene) at a temperature of approximately 900° F. The valves then may be washed in water and thereafter preferably further cleaned by acid pickling. An example of a suitable acid pickling bath is an aqueous solution containing about 2% hydrofluoric acid, 7% sulfuric acid and 10% nitric acid. In some instances the valves may require only a simple degreasing treatment in a chlorinated solvent prior to the aluminum coating and alloying operation. Mechanical cleaning methods, such as grit blasting, sand blasting, etc., may be employed in some cases to supplement chemical treatment.

The steps of degreasing and pickling the valves are not always necessary, however, particularly where the valves are heated in a fused salt preparatory to the actual aluminum coating step since this treatment will provide the valve with a clean surface unless it is exceptionally contaminated initially.

After the valves have been cleaned, the portions thereof which will be contacted by aluminum but which are not to be coated thereby may be treated with an appropriate stop-off coating to prevent any aluminum from bonding

to or alloying with the base metal at such surfaces. A suitable stop-off material for this purpose is a sodium silicate solution, such as an aqueous solution containing approximately 20% to 50% sodium silicate. This step is not essential to the success of the process, however, and merely omitting to degrease or pickle selected areas of the waves frequency will prevent the aluminum from adhering to these areas.

Normally, any suitable poppet valve material may be satisfactorily provided with a thin protective coating layer in accordance with the present invention, and this coating can be applied particularly effectively to the typical ferrous base materials used in valves of internal combustion engines. In the case of aluminum coated steel valves the interfacial layer which is formed next to the steel is complex iron-aluminum. However, the process also can be successfully employed to aluminum coat non-ferrous metals having a relatively low heat of reaction with aluminum, such as titanium and titanium base alloys, nickel base alloys and molybdenum and molybdenum base alloys. The process is generally not recommended for coating metals having a very high solubility in aluminum.

The aluminum with which the valve head is coated can be applied in many forms, such as a stamped ring or washer, an aluminum wire wrapped around the valve stem, and aluminum powder applied as a paste or as a molten metal spray. The latter is commonly referred to as metalized coating. An example of the aluminum paste or paint which may be used in accordance with the invention is a mixture of aluminum powder with suitable amounts of a vehicle, such as low ash content lacquer or resin solution, liquid lucite or a water solution of salt flux. If a salt flux is mixed with the aluminum powder to constitute the paste, it is advantageous to employ a salt flux which is capable of fluxing or cleaning the steel. Hence an aqueous solution of the same salt which is used as the fluxing or heating bath hereinafter described may be advantageously employed as a vehicle for the aluminum powder. Moreover, a combination of resins or lacquers, salt powders and organic liquid vehicles may be mixed with aluminum powder to form the desired paste.

Vinyl resins and acrylic resins are among the lacquer or resins which may be used in the aforementioned paste or spray. The lacquer identified as Binder Solution B–9571, currently manufactured and sold by Pierce & Stevens, Inc., is an example of an appropriate resinous binder. This type of binder normally contains about 4% or 5% solids and 95% solvent. The percentage of the solid resinous constituents is not as important as the volatility of the solvent, however, since high volatility is required to permit rapid drying of the paste after it has been applied to the valve. Good results are obtained when approximately 30% to 50% by volume of aluminum powder, preferably between 200 and 400 mesh, is mixed with 10% to 20% by volume of binder solution and about 30% to 50% by volume of an appropriate thinner or solvent. Acetone or other conventional commercial thinners may be employed. It will be appreciated, of course, that the above ranges of the constituents in the paste composition are not critical and that a very wide variation in the composition may be used to obtain satisfactory results.

In accordance with a preferred embodiment of the present invention, an aluminum paste or paint is applied to the surfaces of the valve or other article. A heating operation is thereafter employed to uniformly distribute the aluminum over the surfaces to be coated and to securely bond the coating to these surfaces. More specifically, after the paste has been applied to the valve by any satisfactory means, such as by brushing, spraying or immersion steps, the valve is immersed in a molten salt flux to a depth sufficient to cover the paste and the portions of the valve to be coated. The paste should be allowed to dry before immersing the valve in the salt so as to avoid introducing volatile matter into the hot salt.

Referring to the drawing, the poppet valve **10** shown in FIGURE 1 is preferably immersed to the approximate depth indicated by the broken line *a—a*. In this position, the head **12** and neck **14** of the valve, as well as the paste **16**, are completely below the surface of the molten salt. The valve is retained in the salt bath for a period of time sufficient to permit the hot salt to melt the aluminum paste and cause the molten aluminum to be distributed in a thin layer over the surfaces of the valve to be coated. Satisfactory results are normally obtained if this immersion period is of sufficient duration so that the immersed article is at a temperature of at least 1275° F. for a few seconds to approximately 90 seconds. However, for poppet valves and other articles of similar size, it is preferred that the valve be retained in the salt for at least 15 seconds after it has reached this temperature. Under these circumstances, a heating and fluxing period in the salt of about 45 seconds to 90 seconds is typical.

A suitable salt flux for aluminum coating operations is described in Patent No. 2,569,097 Grange et al. Hence, it is preferred to use a fused salt bath consisting, by weight, essentially of approximately 37% to 57% KCl, 25% to 45% NaCl, 8% to 20% Na_3AlF_6, and 0.5% to 12% AlF_3. Such a salt flux should be maintained at a temperature of approximately 1275° F. to 1400° F., a bath temperature between 1325° F. and 1375° F. being most desirable.

After the aluminum on the valve has been melted by immersion in the salt bath or other appropriate means, the valve should be rotated or vibrated to properly distribute the aluminum over all the valve surfaces which it is desired to coat. Rotation or reciprocation, particularly rapid vertical oscillation, of the valve is effective in breaking the surface tension effect of the aluminum and spreading of the aluminum over the valve surfaces. For example, rotation of a poppet valve at a rate of 150 r.p.m. has proved to be successful. However rapid rotation may have the disadvantage of distorting the valve head under some circumstances, and most satisfactory results are produced if the fluxed valve having the coating of molten aluminum thereon is rapidly reciprocated in a direction longitudinally of the axis of valve stem 18. Hence, it has been found that such reciprocating motion having an amplitude of approximately ½ inch at a frequency of about 60 cycles per minute is satisfactory. Amplitudes less than 0.005 inch with a 60 cycle per second frequency may also be used, however, and produce excellent results. The agitation period need only be very short, usually ranging from a few seconds to about 90 seconds. Depending upon the size and complexity of the article being aluminum coated, an agitation period between approximately 5 seconds and 60 seconds is preferred.

Although some distribution of the coating metal is possible if this agitation occurs immediately after withdrawal from the salt bath, optimum results are obtained if the valve is agitated in the foregoing manner while still immersed in the fused salt. Vibration in air results in a somewhat more irregular coating because of rapid cooling of the aluminum coating and is therefore not recommended for applications which require a very precise fit between the coated areas and mating parts.

If desired for particular applications, any access aluminum on the valve seat facing which contributes to nonuniformity of the coating may be removed by means of an air blast. This step is usually not necessary, however, and the omission thereof is one of the principal advantages of the present invention. Even if the air blast is omitted, the valve is provided with an extremely thin and uniform coating of aluminum bonded to the base metal by an intermediate extremely thin and uniform layer of an alloy of aluminum with the base metal.

Obviously, if the aluminum coating is sufficiently uni-

form after agitation in the salt bath, the valve may be air cooled directly after removal from the salt flux. It is preferable in most instances to air cool the valve below 800° F. followed by a water quench. If maximum smoothness of the aluminum coating is not of prime importance, the coated article may be quenched in water before the aluminum has solidified. However, this latter procedure generally is not preferred. In either event the valve should be washed in water to remove adhering salt.

It should be noted that this procedure utilizes the fluxing action of the salt even though the areas of the valve to be coated are covered with aluminum paste when the valve is dipped into the salt flux. This occurs because the paste comprises a multiplicity of small globules which permit the salt to contact the base metal to a sufficient extent to provide proper fluxing.

Alternatively, rather than applying a thick paste by means of a brush, the paste may be applied in the form of a thinner "paint" by spraying. As hereinbefore indicated, the aluminum also may be applied as a metal spray in which fine globules of hot, molten aluminum are sprayed against the article to be coated. If molten metal spraying is employed, it is normally desirable that the base material have a relatively rough surface in order that the aluminum will properly adhere to it.

In the case of a poppet valve, its seating face may be coated with aluminum by applying the paste or spray directly to this face or to the neck or throat of the valve. A preferred location of the aluminum paste is shown in FIGURE 1 wherein this paste **16** is applied as an annular layer which overlaps both the seating face **20** of the valve and a portion of its neck **14**. However, when the aluminum is applied in the form of a solid ring or wire in the manner hereinafter described, its position is more critical because of the problem of premature melting of the aluminum.

Referring now to FIGURE 2, a modification of the above procedure may be employed using an aluminum wire, washer or ring member **22** which is positioned around the valve stem **18** and serves as a source of aluminum for coating the valve. The ring may be fairly tightly fitted around the valve or it may be positioned loosely around the stem and permitted to drop to a point where it is supported by the outward curvature of the neck **14** of the valve. Locating the aluminum ring at a measurable distance above the valve seating face **20** permits selective or localized preheating and fluxing of the steel head and neck of the valve before the ring is melted.

Following the locating of the aluminum member on the valve stem, the valve is immersed in a molten salt flux, such as the one hereinbefore described, so as to normally completely cover the valve head and part of the stem. It is desirable, however, not to dip the valve in the molten salt flux a sufficient distance to immerse the aluminum washer or ring member **22**. The preferred level of the salt flux when the valve is immersed in it for preheating purposes is indicated by the broken line *b*—*b* in FIGURE 2. In this position the aluminum ring will not contact the molten salt and will not melt. If the ring melts before the valve head reaches the proper temperature, a sound bond between the aluminum and base material of the valve will not be produced. Of course, other methods of rapid selective heating of the valve head might be used which will permit the positioning of the aluminum ring closer to the areas which are to be coated.

After the valve head has reached a temperature of approximately 1275° F. to 1400° F., the valve is immersed further in the hot salt to a depth sufficient to envelop the aluminum ring **20**. The level of the salt with respect to the valve during the aluminum melting step is indicated by the broken line *c*—*c* in FIGURE 2. The valve is retained in this new position with the ring beneath the surface of the salt flux long enough to permit the fused salt to melt the ring and cause the molten aluminum to run down the neck of the valve onto its seating face. When the ring has completely melted, the valve is vibrated, preferably in the molten salt, in the manner hereinbefore described to properly distribute the aluminum as a thin coating and to remove excess aluminum.

In order to successfully aluminum coat by means of the last described procedure, the base metal should be completely fluxed and heated to proper temperature before the aluminum on the article to be coated is melted. For example, if a valve is not completely fluxed and heated to a sufficiently high temperature, partial wetting of the steel results and only localized, spotty alloying action occurs to form a chemical bond. Moreover, if the aluminum is permitted to be distributed over the valve head before the latter is adequately fluxed, the aluminum may shield the steel from beneficial fluxing action by the fluxing medium in which it is being heated.

Regardless of which of the above procedures is employed, the length of time the valve is permitted to remain in the salt bath for the purpose of melting and distributing the aluminum is dependent upon the size and shape of the arcticle being coated. In the case of typical poppet valves for internal combustion engines, a heating period of approximately one minute in the salt bath followed by a vibration period of one minute in the bath has proved to be highly satisfactory. On the other hand, if the article to be coated is first preheated in a furnace or by other suitable means before applying the aluminum, the dipping time in the salt can be appreciably reduced. For example, such preheating of a poppet valve to a temperature of 1000° F. or 1100° F. permits the use of a salt dip of only a few seconds duration. Hence, the dipping period may be defined as that time required to raise the article to be coated to a temperature between approximately 1275° F. and 1400° F. It is never necessary to preheat the valve seat when aluminum paste or spray is used, however, because the problem of non-uniform melting is not present as it is when an aluminum ring or wire is used. In the latter case, since there is a danger that the ring will fall from the valve stem after it has partially melted, preheating with the molten salt or by other appropriate means is an important step in the process.

Of course, the size of the aluminum ring, amounts and composition of the aluminum paste or the thickness of the aluminum applied to the valve governs the thickness of the aluminum coating. As previously explained, since the valve seating face normally is the only portion of the valve in which the aluminum coating layer thickness is critical, it is this area which determines whether excess aluminum has been deposited. As an example of the proper amount of aluminum to be used, an aluminum ring member which weighs approximately 0.1 to 0.25 gram appears to be appropriate for coating a typical poppet valve of an automobile engine. Use of a ring of this size produces no obvious irregularities in the aluminum overlay and does not require removal of excess aluminum by a blowing operation.

In some instances, however, it may be desirable to apply aluminum in an amount exceeding the quantity actually used as a coating layer because of difficulty in distributing the metal over all of the surfaces during the coating or alloying step. The excess coating metal may be removed by mechanical or pneumatic methods, as indicated above.

The above-described aluminum coating procedures provide the surfaces of the article treated with a uniform aluminum coating having a thickness which can be carefully regulated during processing. In turn, the thickness of the intermediate aluminum-iron alloy layer may be controlled, and it is this layer which is primarily determinative of the life of the valve. Moreover, not only are the resultant aluminum overlay and intermediate aluminum-iron alloy layer uniformly thin, but the dimensions of the seating face of the valve so processed will not be disadvantageously affected during removal of the surplus molten coating material or salt flux. In the photomicro-

graph shown in FIGURE 3 the base metal of the valve is indicated at **24**, while **26** indicates the alloy of aluminum with the base metal and the outer layer **28** of aluminum.

The aluminum-base metal alloy layer **26** produced normally ranges from about 0.0005 inch to 0.0015 inch in thickness, while the aluminum overlay **28** does not exceed approximately 0.004 inch. In the case of automobile poppet valves, it is preferred to have the outer aluminum layer between 0.0005 inch and 0.0015 inch thick, resulting in a combined thickness of the iron-aluminum alloy layer and the aluminum overlay of approximately 0.001 inch to 0.0025 inch. A coating layer of this thickness has demonstrated superior yielding characteristics when the valve seating face is "pounded in" during service. Small depressions in the seating face of the valve caused by engine deposits which become lodged between the valve seating face and valve seat during operation remain protected by the surface alloy layer.

The uniform thin coating thus provided on a poppet valve head eliminates the possibility of run-down of the coating metal due to melting while the valve is in operation in an engine. An interference fit at the valve seating area might otherwise result. Moreover, a non-uniform coating prevents proper installation of a valve in an engine because the valve seat facing does not conform to the valve seat.

Of course, the distribution or thickness of the coating on the valve end face is not critical from the standpoint of fitting with mating parts since this portion of the valve does not contact any part of the engine in which it is used. The only problem therefore is that of flaking off or spalling of the coating on the head end face of the valve if this coating is excessively thick.

Certain variations may be made in the processing procedure described above without departing from the principles of this invention. Thus, where the nature of the article to be coated permits, this article or appropriate portions thereof may be heated in a furnace under an air or protective atmosphere or may be flame heated or induction heated. In order to obtain a proper bond between the aluminum and base metal to be coated, a reducing or inert atmosphere is required unless a salt flux is used on the surfaces to be coated. Likewise, these articles may be coated with flux during this heating step or they may be heated prior to the application of the salt flux. When these latter procedures are employed, it is not necessary to preheat the valve or other article in a fused salt flux bath, as described above, but the molten salt should be employed only for the purpose of fluxing the valve surfaces to promote the proper adhesion of the aluminum to the steel. Of course, these alternative methods of heating are dependent upon the fluxing ability of the salt used and/or the ability of the atmosphere to protect or chemically clean the steel surfaces before molten aluminum contacts it. When the valve or other article is heated outside a salt flux bath in the foregoing manner, the aluminum must still reach a temperature between approximately 1275° F. and 1400° F. in order to effectively coat the article.

In light of the specific procedures described above, it is readily apparent that the two principal and essential steps in carrying out the present invention are the application of aluminum to the valve or other article to be coated and the heating of this article in such a manner as to cause the aluminum to melt, to flow evenly over the surface to be protected, and to become securely bonded thereto. Such an article is thereby selectively coated with aluminum by a rapid, simple and inexpensive process which provides a continuous and chemically alloyed coating without immersing the article in a molten bath of aluminum.

It should also be noted that the invention in its broader aspects comprehends, as a source of aluminum or aluminum alloy, the use of stamped aluminum shapes, aluminum wire, aluminum powder mixed with a suitable organic vehicle to form a paste, aluminum powder mixed with a salt flux and water to for a paste, and aluminum powder mixed with a salt flux and an organic vehicle.

While this invention has been described by means of certain preferred embodiments and specific examples, it will be understood that the scope of the invention is not to be limited thereby except as defined in the following claims.

We claim:

1. The method of coating a ferrous metal object with aluminum, which method comprises the steps of cleaning and roughening the surface to be coated, spraying a coating of liquefied aluminum on said surface, displacing air from contact with said coated surface and covering the same with an oxyegn-free inert gas, and while maintaining said covering of inert gas, heating the object to a temperature above the melting point of aluminum to fuse said aluminum coating into a substantially impervious layer securely bonded to the surface of said object.

2. A method of coating a base metal having a relatively low heat of reaction when in contact with molten aluminum with a coating metal containing at least 80% aluminum, said method comprising spraying said coating metal onto said base metal, and thereafter heating said article in an oxygen-free inert gas at a temperature within the range between about 1275° F. and 1400° F. for a time sufficient to cause the coating metal to fuse into a substantially impervious layer securely bonded to the surface of said base metal.

3. A method of coating a base metal having a relatively low heat of reaction when in contact with molten aluminum with a coating metal containing at least 80% aluminum, said method comprising spraying said coating metal onto said base metal, and thereafter heating said article in an oxygen-free inert gas at a temperature and for a time sufficient to cause said coating metal to fuse into a substantially impervious layer securely bonded to the surface of said base metal.

4. A method of coating a base metal having a relatively low heat of reaction when in contact with molten aluminum with a coating metal containing at least 80% aluminum, said method comprising spraying said coating metal onto said base metal, and thereafter induction heating said article in an oxygen-free inert gas at a temperature within the range between about 1275° F. and 1400° F. for a time sufficient to cause the coating metal to fuse into a substantially impervious layer securely bonded to the surface of said base metal.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,065,107 November 20, 1962

Dean K. Hanink et al.

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

Column 1, line 36, for "lift" read -- life --; column 2, line 3, for "stull" read -- still --; column 3, line 7, for "waves frequency" read -- valves frequently --; column 4, line 65, for "access" read -- excess --.

Signed and sealed this 21st day of May 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents