A method for the manufacture of a corrosion-resistant aluminum metal-coated ferrous product and particularly a product composed of a zinc-coated ferrous metal substrate having superimposed thereon a coating of aluminum metal. The product prepared therefrom is characterized by having an intermediate layer of phosphate crystals of a minimum thickness sufficient to prevent interaction between the zinc undercoating on the ferrous metal substrate and water passing through the superimposed aluminum metal surface coating. The interposing layer of phosphate crystals has a critical maximum thickness such that not more than 100 milligrams of phosphate crystals is distributed over each square foot of surface area of the zinc ferrous metal substrate. Optimally, the interposing crystalline phosphate layer has a thickness such that 10 to 30 milligrams of phosphate crystals are distributed over each square foot of zinc ferrous metal substrate. The method of applying the said corrosion-resistant aluminum coating to the zinc ferrous metal substrate comprises: (a) contacting said zinc-coated ferrous metal substrate with a solution containing phosphate ion for about 2 to 15 seconds at a processing temperature of about 70° to 100°F. and (b) subsequently applying thereto a superimposed overcoat of an aluminum metal and bonding the composite coatings and substrate into a corrosion-resistant product.

20 Claims, 1 Drawing Figure
A METHOD FOR APPLYING CORROSION-RESISTANT COMPOSITE COATING TO FERROUS METALS AND PRODUCT RESULTING THEREFROM

BACKGROUND OF THE INVENTION

The coating of sheet steel and other steel and ferrous metal articles with zinc as by hot-dip galvanizing, electroplating, and vapor deposition techniques is generally employed by steel manufacturers in an effort to reduce corrosion or the like deterioration of the surface of the ferrous metal. In operation the zinc coating preferentially corrodes and thus protects the surface of the ferrous metal from corrosion. Necessarily in the course of such protection the zinc coating is dissipated after a period of use. The short usage life of zinc-treated steel, for example, may be illustrated by inspection of steel surfaces subject to contact with salt or brine spray which, unless a disproportionate thickness of zinc is employed, greatly abbreviates the protective life of the zinc coating.

In an effort to gain the anticorrosive advantages of a zinc coating on a ferrous metal substrate, protect the zinc from rapid erosion and improve the composite surface as a paint base, it has been suggested to apply to the surface of the zinc steel substrate a protective metal overcoat. This overcoat is principally composed of aluminum metal applied preferably by vapor deposition although other means such as spray, electroplating, or other conventional means of coating aluminum on substrates can be employed.

While such protective overlay or overcoating of aluminum will generally adhere initially with excellent results to the zinc steel substrate, subsequent exposure of the composite to the environment, particularly where water is constantly contacting the surface of the aluminum, small quantities of water tend to work their way through the fine microscopic pores of the aluminum and come in contact with the zinc undercoat at the interface or juncture between the two metals. Since the zinc and aluminum metals have different positions in the electromotive series they will accelerate any water vapor or water present to interreact with zinc in the nature of galvanic corrosion. This reaction gives rise to the release of gaseous reaction products which cause a bubbling or blistering to weaken the surface coating of aluminum. It is believed that the basic reason for such blistering which occurs at elevated temperatures over a short duration or at room temperature over a longer period of time is the water vapor contacting the zinc layer to form hydrogen gas which evolves and works its way to the surface to blister the aluminum overcoat. An attempt to prevent such blistering by the application of an intermediate chromate coating or later of copper proved unsuccessful because it interfered with the adherence of the aluminum overlay coating to the zinc-ferrous metal substrate. Coating with chromate ions while relieving the blistering formation somewhat, also presented problems of adherence of the metalized layers to one another and resulted in poor bonding of the aluminum overlay to the zinc-ferrous metal substrate. It became an object of the present invention, therefore, to develop a means for the prevention of blister formation of aluminum-zinc-ferrous metal composite structures without reducing the adherence of the coatings in the composite structure to one another.

BRIEF DESCRIPTION OF THE INVENTION

The present invention, therefore, describes a method for the manufacture of a corrosion-resistant aluminum metal-coated zinc-ferrous metal substrate having improved resistance to aqueous attack and consequent blistering of the surface coating of aluminum metal. The practice of the method of the invention results in a product characterized by having an intermediate layer of phosphate crystals of a minimum thickness sufficient to prevent interaction between vapor penetrating through the aluminum overlay and the zinc coated portion of the substrate. The interposing layer of phosphate crystals has a critical maximum thickness such that not more than 100 milligrams of phosphate crystals are distributed over each square foot of surface area of the zinc-ferrous metal substrate. It has been found that within these parameters, contact between the water vapor and the zinc metal has been effectively prevented at the same time that the adherence between the zinc-ferrous metal substrate and the aluminum metal overlay has been maintained and in some instances improved.

In the practice of the method of the present invention it has been found that an optimal thickness of the crystalline phosphate coating can be obtained such that the phosphate layer has a thickness corresponding to the uniform distribution of about 10 to 30 milligrams of phosphate crystals over each square foot of zinc-ferrous metal substrate to which it is applied. The method for applying the said corrosion-resistant composite coating to the said zinc-ferrous metal substrate comprises: (a) contacting said zinc-coated ferrous metal substrate with a solution containing phosphate ion for about 2 to 15 seconds at a processing temperature of about 70° to 100° F. and (b) subsequent applying thereto a superimposed overlay coating of aluminum metal and bonding the composite coatings and substrate into a corrosion-resistant product.

To these and other ends, the method of the present invention contemplates establishing an adherent coating of zinc metal on a steel substrate in a conventional manner; thereafter applying to the zinc-coated surface a thin coating of phosphate crystals and thereafter depositing a further thin coating or overlay of aluminum by means of vapor deposition or other means of application of aluminum coatings familiar to the art.

It has been found that composite zinc-coated steel articles produced in such manner exhibit a greatly increased resistance to corrosion in general and in particular demonstrate greatly increased duration of effective protection against breakdown and corrosion of the zinc coating and steel substrate as compared to that corrosion protection afforded by the known zinc-coated aluminum overlay-coated steel products of the prior art. The improvement in corrosion resistance imparted by the present process is believed to be due to the imposition of a barrier layer of phosphate crystals between the aluminum overlay and residual on the ferrous substrate. This barrier layer prevents water or water vapor which may in some cases penetrate the fine pore structure of the aluminum overlay coating from coming into contact with the zinc layer. The reaction between the water vapor and zinc metal to form zinc oxide and hydrogen gas is thus inhibited and the generation of the gaseous reaction product arrested. This in turn acts to prevent a blistering or bubble formation in the aluminum overlay coating which is caused by the reaction of such gaseous reaction products and consequent corrosion or breakdown of the aluminum surface coating.

In the practice of the method of the present invention, the zinc-steel substrate manufacturer will proceed along lines conventional to the art. Hence the zinc coating established on the steel substrate may be obtained by hot-dip galvanizing or electroplating of the steel with zinc metal. In hot-dip galvanizing the cleaned steel surface is generally immersed in a body of molten zinc to create a surface layer of zinc which solidifies as a surface coating thereon. Electroplating of zinc proceeds by immersing the steel surface in an electrolytic bath containing a zinc source material such as zinc sulfate and passing a direct electric current through the bath to plate an adherent coating of zinc onto the surface. The resulting zinc coating may have a thickness of the order of 20 to 1,500 microinches or more. In any event this coating technique is well known to the art and is not claimed "per se" as part of the present invention.

At this point in the process the zinc-coated ferrous article to be protected is treated with a phosphate solution for a sufficient period of time and at a suitable reaction temperature to effect deposition of from 10 to 60 mg./ft.² of phosphate coating over each area of the article being treated. A preferred method of phosphate treatment involves dipping the zinc-coated steel sheet into a phosphating solution for about 10 to 60 seconds preferably for from 70° to 120° F. and preferably 20 seconds at a bath temperature of 90° F. The result after drying is the deposition of a thin coating of crystal-
lized phosphate over the layer of zinc sufficient to block any water vapor coming through the pores of the aluminum overcoat which is applied over the phosphate layer.

The atmosphere is then protected from further oxidation by applying a thin film of aluminum overcoat to the surface of the zinc-phosphate coating. The film thickness is determined by the rate of vapor deposition and exposure of the surface thereto.

A specific illustration of a vacuum metallizing technique suitable for use in depositing an aluminum overcoat in a furnace is shown in U.S. Patent No. 2,959,494. While in the aforesaid patent the aluminum coating is deposited on a bare steel substrate, the general technique for vapor deposition on the coated substrate of the present invention is substantially the same. The technique illustrated in the patent involves a vacuum metalizer which is evacuated prior to aluminum deposition. The procedure is essentially four-step and includes a first step of pumping the chamber to a vacuum of 200 microns of mercury. The atmosphere remaining after a pumpdown must not contain organic vapor. The surface of the substrate is degassed by a high-voltage discharge. After this discharge, a next step of the pumpdown procedure carries the vacuum to about 510 microns pressure. Aluminum is then vaporized from a suitable heated surface which is constantly fed with metallic aluminum. If desired, the aluminum may be vaporized by means of an electron beam vaporizing apparatus and technique wherein the aluminum source is positioned in the vacuum chamber in the path of a beam of electrons from a suitable electron source with an appropriate voltage applied between the electron source and the aluminum source so that the electron beam vaporized aluminum from the latter source results in deposition on the substrate to be coated. This latter technique is also known to the art and is not claimed herein as a unique contribution but is described as part of the overall improved technique or formation of a corrosion-resistant composite coating. In addition to the aforesaid vacuum metallizing technique, another technique which may be employed in the aluminum coating step of the present process is the vacuum metallizing system described in U.S. Patent No. 3,117,887 which The aluminum which is caused to evaporate from the surface of the heated block ultimately deposits on the substrate which passes by within the confines of the vacuum chamber.

The product of the present invention may be generally described as a sheet, strip or other shaped article which comprises a ferrous metal substrate upon which are deposited in ascending order a coating of zinc metal, a thin coating of phosphate crystals and finally an overcoating of a thin layer of aluminum. The article produced derives structural strength from the ferrous metal substrate and protection from corrosion and other surface deterioration by the other coating members in the composite. The zinc coating itself provides a measure of corrosion resistance to the steel base. The phosphate coating protects the zinc coating from galvanic corrosion and isolates it from contact with aqueous vapors or liquids. The aluminum coating which overlies the surface protects all of the materials which underlie it from surface abrasion as well as offering an inert surface to sources of oxidative deterioration which can pose problems to the use of the composite. Upon final application of the aluminum coating, this same acts to bond the two composite structure together onto one article which is highly resistant to corrosive attack. A presently preferred range of values of thickness for the vapor-deposited aluminum overlayer varies between about 5 microinches and about 100 microinches with the narrower range of 30 to about 60 microinches being preferred. The thickness of the phosphate crystal coating is generally such that not more than 100 milligrams of phosphate crystal covers each square foot of surface area. The adherent zinc coating is generally of the thickness of 15 microinches to 300 microinches.

After the composite material as described above has been prepared, the aluminum-coated steel surface may, if so desired, be coated with an additional layer of a chromate solution. As is known to the art, this particular surface treatment renders the aluminum-coating more receptive to the application of paint and other organic coating materials. A simple example of a well-known chromate surface treating agent is a solution of potassium dichromate which, when applied to the surface of the aluminum-coated article, does impart some beneficial surface qualities thereto.
In terms of the present invention, the effect of the treatment of zinc-coated steel with the phosphate composition, prior to the application of the aluminum overcoat has been ascertained and its parameters defined by testing a series of samples of zinc-coated steel with the objective of obtaining not only protection against aqueous attack and corrosion but also satisfactory adherence between the various members of the composite. The samples tested included panels having aluminum coatings 15, 30, 45 and 60 micrometers thick deposited over phosphate coatings of various thicknesses ranging from less than 5 micrometers per square foot to as high as 120 milligrams per square foot. All of the panels were zinc-coated in the same manner and the surface cleaned in such a manner as to reduce the variables to the characteristics of the phosphate coating. For purposes of comparison, the phosphate coating was comparatively evaluated against a chromate ion coating and a copper coating, both of the latter two coatings being proven to be unsatisfactory for reasons of poor corrosion resistance or that the thicknesses required for improving the corrosion resistance exhibit an unsatisfactory prevention of adherence of the aluminum overcoat to the zinc-steel substrate.

The testing procedures employed were standard ASTM test method D 714-56. The evaluation of the blistering effect of steam on representative test samples which were placed in a pressure cooker and heated, were conducted in the presence of water until a pressure of 10 pounds per square inch (steam pressure) was developed. In conjunction with this, the standard ASTM blister rating scale was employed to evaluate the relative effect of the water vapor upon the test samples analyzed. The adherence of the aluminum coating to the underlying substrate was evaluated by pushing a ball through the steel until the steel ruptured. Scotch tape was then applied to the drawn area and rapidly removed. Poor adherence was concluded when aluminum adhered to the tape and came off with it upon its removal.

The results of these various tests demonstrated that for all thicknesses of aluminum coating the presence of the phosphate crystalline layer interposed between the zinc-ferrous metal substrate and the aluminum overcoat prevented the blistering of the aluminum overcoat no matter how long it was exposed to the steam environment. In the case of chromate and copper coatings applied in comparable thicknesses to the phosphate coating such that no less than 10 milligrams per square foot of any of the coatings were applied to the substrate, the chromate and copper coatings in some instances did prevent blistering but in those instances interfered with the adherence of the aluminum overcoat to the substrate. In contrast, phosphate crystalline coatings applied within a thickness range of 10 to 100 milligrams per square foot gave both good adherence and blister-free surfaces. If the coating thickness was diminished to below the lower level of this parameter, blisters developed. On the other hand, if the coating thickness increased above the upper parameter, there was a gradual loss in adherence of the aluminum coating to the zinc coating.

Although the method of the invention has been described above as involving the application of a zinc coating to the steel base by means of conventional electroplating or hot-dip galvanizing techniques, it is within the concept of the invention to apply other known methods such as vacuum vaporization of the zinc which zinc vapor is then directed to the surface of the steel sheet in a vacuum chamber in a manner analogous to that employed with the vacuum deposition of aluminum described above. In general, the layers of zinc, regardless of how they are deposited, normally comprise about 15 to 300 micrometers of zinc and the aluminum layers may vary all the way from 5 to 100 micrometers in thickness depending to some extent upon the economics and other operating conditions. In any event, regardless of the relative thicknesses of the zinc and aluminum coatings, so long as the parameters of the phosphate treatment method are observed, there will be sound adhesion between all the layers of the composite regardless of their protracted exposure to the elements. The accompanying drawing shows an illustration of the novel products of the invention as produced by the process of the invention, a diagrammatic prospective enlarged view of a portion of a steel sheet produced with a zinc coating, an interposing phosphate crystal coating and an overlay coating of aluminum metal. In the preparation of such an article, the ferrous metal sheet 10, which is preferably a steel sheet in the form of a cold rolled strip is first coated with an adherent layer of zinc 11 on both opposing faces by one of the conventional coating techniques. Thereafter, a crystalline phosphate coating 12 is placed over the zinc layer. Finally, an overlayer of aluminum 13 is applied by any one of a number of conventional aluminum treating techniques such as vacuum metallizing. It is to be understood that this sketch is purely for purposes of illustration of the general processing technique and a number of variations can be involved where either one or both sides may have varying thicknesses of coatings or in some instances one side may have additional surface conditioning treatment, all of which are within the general concept of the invention.

The following examples are set forth to illustrate specifically a preferred method of practice of the invention. The broad definition of the process and products produced by this unique process is set forth in the several appended claims and it is with reference to these claims that the scope of the invention must be measured.

**EXAMPLE I**

Small panels of 1,010 mild steel coated with zinc metal coating of 174 microns on the bottom side and a zinc coating of 203 microns on the side were cleaned with F-11 cleaner (concentration 2 oz. per gallon) at 170°F. to remove any residual impurities.

They were then sprayed at room temperature (75°F.) with a 15 percent phosphating solution (Parker Rustproof 33A) for 8 seconds at 75°F. The coating was then dried so as to evaporate any water and leave a uniform coating of phosphate crystals in amount of 20 milligrams of crystals per square foot of surface area.

These strips were then plated with vapor aluminum to give an aluminum coating of approximately 50 micrometers of aluminum metal thereon. Upon testing for blister rating in the steam chamber and testing for adherence, both test results indicated an excellent result.

**COMPARATIVE EXAMPLES A AND B**

A. The following example was run to demonstrate the criticality of the parameters of the process of the invention.

Small zinc-coated steel test panels similar to those employed in preceding Example I were cleaned using Parcolene 342 cleaner, (¼ ounce per gallon) at 160°F. to remove surface residual impurities in standard cleaning procedure.

They were then sprayed with a 15 percent phosphating solution at 135°F. for 30 seconds, and rinsed with distilled water. The phosphate coating deposited was 216 milligrams of phosphate crystals per square foot of surface area. They were then dipped 3 times in Parcolene 342 cleaner at 160°F. and air dried.

B. This experiment was repeated on other test strips using Bonderite 32 (phosphating solution) instead of Bonderite 33A to the result that 184 milligrams of phosphate crystal per square foot of substrate was deposited. Vapor aluminum was then plated in both samples.

In both cases the evaluation of both sets of test strips indicated that although the phosphate coatings retarded blistering the adherence of the composite was poor. In effect a phosphate crystal layer of 184 milligrams per square foot of substrate is too thick to produce satisfactory bonding between the aluminum, phosphate and zinc-steel layers in the composite formed.

**COMPARATIVE EXAMPLE C**

Zinc-coated steel strips identical to those employed above were given a chromate coating by dipping in a solution con-
3,642,541

The chromate coating itself was observed to have poor adherence to the zinc substrate and was totally unsatisfactory as regards adherence between the aluminum overcoating and zinc-steel substrate. The blister ratings however, while not as good as with the phosphating coating, indicated a blister reducing effect. The chromate coating was hence not usable.

**COMPARATIVE EXAMPLE D**

In an effort to compare the value of a copper coating on the zinc-ferrous substrate in place of either a phosphate or chromate coating, a third set of test strips was dipped in an F-11 cleaning solution, rinsed and immersed in a Rochelle-type copper bath for varying intervals of time. The strips were copper plated at intervals 5, 10, 15 and 20 seconds.

The evaluation of the coated strips when tested in the same ASTM test series concluded that while blister effect was reduced after steam contact, the adherence between the layers of the coated composite was extremely poor.

**COMPARATIVE EXAMPLE E**

To determine the lower level of the parameter of the invention, the zinc-coated test strip was treated with a phosphoric acid solution containing 2.5 milliliters per liter of full strength phosphating solution for treating times of 10 seconds and 40 seconds, respectively. The amount of phosphate crystals thus deposited at the interposing junction between the zinc base and the aluminum overcoat is less than 10 milligrams of phosphate crystals per square foot of surface area of the zinc-ferrous substrate. This test sample when evaluated indicated blistering to a demonstrable degree on the surface of the aluminum layer after exposure to moisture in the steam chamber for 10 minutes.

While the aforesaid several examples and general description of the invention set forth aluminum metal as the surface coating or protective overlay, it is well within the scope of the invention to employ other metals equivalently to aluminum as the surface coating. Such metals as copper, brass, titanium, zinc, chromium, steel, and various alloys of any of these could be employed to replace the aluminum overlay depending on the article to be formed and the use to which it is to be applied. In comprehending the invention it is necessary to include these metals within the scope of the general method and article resulting therefore which is particularly illustrated above.

What is claimed is:

1. A method for applying a corrosion-resistant composite coating to a ferrous metal substrate which comprises:
   a. contacting a zinc-coated ferrous metal substrate with a solution containing a phosphate ion for a period of time and at a solution temperature sufficient to deposit a crystalline phosphate layer of uniform thickness thereon, said layer having a thickness sufficient to inhibit reaction between the zinc layer and any water vapor with which it may come in contact and a maximum thickness such that substantially not more than about 100 milligrams of phosphate crystals are uniformly distributed over each square foot of the substrate treated and
   b. applying thereto a surface coating of at least one metal selected from the class consisting of aluminum, copper, brass, titanium, zinc, chromium, steel and alloys thereof.

2. A method for applying a corrosion-resistant composite coating to a ferrous metal substrate according to claim 1 wherein the crystalline phosphate layer deposited is of zinc phosphate.

3. A method according to claim 1 wherein the surface coating applied in (b) is an aluminum metal coating.

4. A method for applying a corrosion-resistant composite coating to a ferrous metal substrate according to claim 1 wherein the coating comprises contacting the zinc-coated ferrous metal substrate with a phosphating solution for a period of from about 2 to about 15 seconds at a processing temperature of from about 70° to about 130° F.

5. A method for applying a corrosion-resistant composite coating to a ferrous metal substrate according to claim 1 which comprises contacting the substrate with a phosphating solution for a period of about 8 seconds at a processing temperature of about 75° F.

6. A method according to claim 1 wherein said crystalline phosphate layer contains from about 10 to about 30 milligrams of phosphate crystals distributed over each square foot of surface area of the substrate treated.

7. A method for applying a corrosion-resistant composite coating to a ferrous metal substrate according to claim 1 wherein the surface coating of a metal applied in step (b) is applied by vapor deposition.

8. A method according to claim 7 wherein the metal which is vapor deposited is aluminum.

9. A method according to claim 8 wherein the aluminum coating applied as a surface coating has a thickness of about 50 micromiches.

10. A method for application of a corrosion-resistant phosphate crystal coating to a zinc metal substrate which comprises:
   a. applying to the surface of the zinc metal an aqueous phosphating solution comprising free phosphoric acid and a soluble metallic phosphate salt;
   b. maintaining the zinc metal substrate in contact with the aqueous phosphating solution for a sufficient period of time to cause the phosphoric acid to react with the zinc substrate to form an excess of zinc phosphate which precipitates out of solution as a corrosion-resistant phosphate crystal coating on the zinc metal base such that no more than about 100 milligrams per square foot of phosphate crystals are precipitated out of solution on the zinc metal base, and
   c. applying thereto a surface coating of at least one metal selected from the class consisting of aluminum, copper, brass, titanium, zinc, chromium, steel and alloys thereof.

11. A corrosion-resistant composite coated ferrous metal product having interposed between a zinc-treated ferrous metal substrate and a metal overlay coating a layer of phosphate crystals of sufficient minimum thickness to inhibit corrosive interaction between the zinc layer of the substrate and water penetrating through the metal overlay and a maximum thickness such that not more than about 100 milligrams of phosphate crystals is uniformly distributed over each square foot of the substrate treated wherein said metal overlay coating comprises at least one metal selected from the class consisting of aluminum, copper, brass, titanium, zinc, chromium, steel and alloys thereof.

12. A corrosion-resistant composite coated ferrous metal product according to claim 11 wherein the metal overlay is of aluminum metal.

13. A corrosion-resistant composite coated ferrous metal product according to claim 11 wherein the phosphate crystal layer is composed of zinc phosphate crystals.

14. A corrosion-resistant composite coated ferrous metal product according to claim 11 wherein the layer of phosphate crystals thereon has a uniform thickness such that from about 10 to about 30 milligrams of phosphate crystals is distributed over each square foot of surface area of the zinc-coated ferrous metal substrate.

15. A corrosion-resistant composite coated ferrous metal product according to claim 14 wherein the layer of phosphate crystals thereon has a uniform thickness such that about 20 milligrams of phosphate crystals is distributed over each square foot of the surface area of the zinc-coated ferrous metal substrate.

16. A corrosion-resistant aluminum-zinc metal composite coated ferrous metal product comprising:
   a. a steel substrate of sufficient thickness to support a plurality of coatings.
b. a zinc layer deposited thereon which comprises from about 15 to about 300 microinches of zinc;
c. deposited on the surface of the zinc layer and beneath the aluminum overcoat of (d) a layer of phosphate crystals having an approximate thickness of from about 10 to about 100 milligrams uniformly distributed over each square foot of the zinc substrate; and
d. an aluminum overcoat superimposed on the phosphate crystal layer wherein the aluminum metal has an approximate thickness extending from about 5 to about 100 microinches.

17. A coating method comprising applying to the surface of a zinc substrate a coating of phosphate crystals of no more than about 100 milligrams of crystals per square foot of substrate, and applying over the coating of phosphate crystals a coating of at least one metal selected from the class consisting of aluminum, copper, brass, titanium, zinc, chromium, steel and alloys thereof.

18. A coating method according to claim 17, in which there is applied from about 10 to about 30 milligrams of phosphate crystals per square foot of substrate.

19. A zinc-coated article, comprising a zinc substrate coated with phosphate crystals of no more than about 100 milligrams of crystals per square foot of substrate, and an overcoat over the phosphate crystal layer of at least one metal selected from the class consisting of aluminum, copper, brass, titanium, zinc, chromium, steel and alloys thereof.

20. A zinc-coated article according to claim 19, in which there are from about 10 to about 30 milligram of phosphate crystals per square foot of substrate.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,642,541
Dated 15 February 1972

Inventor(s) George A. Shepard

It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

In the Abstract, 7th line from the bottom, after
"the" insert -- said--; Column 2, Line 39, after "overlay" insert --coating
and the zinc coating which underlies the aluminum overlay--; Column 3, Line 21, after "sodium" insert
--hydroxide--; Column 4, Line 33, after "which" insert
--involves evaporation of aluminum metal from a plate or block
which is maintained at aluminum vaporizing temperature by
electrical resistance heating.-- Column 5, Line 67 "vent" should be --event--; Column 9, line 11 omit "C".

Signed and sealed this 1st day of May 1973.

(SEAL)
Attest:

EDWARD H. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCALK
Commissioner of Patents