## Patented Sept. 25, 1951

## 2,569,097

# UNITED STATES PATENT OFFICE

#### 2.569.097

## METHOD OF COATING FERROUS METAL WITH ALUMINUM OR AN ALUMINUM ALLOY

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### No Drawing. Application February 20, 1951, Serial No. 211,977

### 17 Claims. (Cl. 117-52)

This invention has to do with the coating of steel or other ferrous metal with aluminum or an aluminum base alloy. This application is a continuation-in-part of our copending application Serial No. 762,830, filed July 22, 1947, now forfeited.

Among the advantages of aluminum coated steel are good resistance to acid attack and good resistance to heat.

Methods have been proposed heretofore for 10 coating steel with aluminum by hot dipping. However, prior art methods of which we are aware have been impractical commercially or have been complicated and the coated product produced thereby quite expensive. In addition, 15 be one capable of dissolving aluminum and iron brittle iron-aluminum compounds are formed between the steel and aluminum which materially limits the formability of this composite heatresistant material. Accordingly there has been only a limited commercial use of hot dipped 2 aluminum coated steel.

The primary object of the present invention is to provide a simple, practical and inexpensive process of producing an aluminum or aluminum base alloy coated ferrous metal product of high 25 1180° F.

Another object of the invention is to provide a process of forming a composite product or article comprising steel coated with aluminum or an aluminum base alloy that has a high degree of  $_{30}$ formability as compared with the products produced by prior methods.

Other objects and advantages of the invention will become more apparent from the detailed description which follows.

Steel or ferrous metal of any shape can be coated with pure aluminum or aluminum base alloys by the method of this invention. The process may be a continuous one if desired, especially when the metal being coated is sheet, wire 40or rod stock.

The steel or other ferrous metal to be coated is preferably first degreased in any suitable manner as by means of an alkali cleaner or by use of suitable solvents. After degreasing the steel, if 45 severely rusted or scaled, it is preferably pickled in a water solution of hydrochloric acid in the known and accepted manner of such acid cleaning. After pickling, the steel or other ferrous metal may be immersed in a flux such as one 50 composed of 32 parts of zinc chloride, 8 parts of ammonium chloride and 60 parts of water, all measurements by weight. The foregoing flux is given as a typical example of a zinc chloride type flux which may be used. After treating in the 55

2

steel fluxing medium just described, in accordance with a preferred embodiment of our invention, the steel or other ferrous metal is immersed in a molten salt floating on top of a molten aluminum or aluminum base alloy coating bath. The salt is maintained at a temperature somewhat above the melting point of the aluminum or the aluminum base alloy. The steel or other ferrous metal is left in the fused salt a sufficient time to heat the metal to or above the melting point of the aluminum or aluminum base alloy. The heated steel or other ferrous metal is passed from the heated salt to the molten aluminum or aluminum alloy bath. The molten salt bath must oxides. The following is a specific salt bath that

Dotossius	Octopolyme -1-1- 11 (		
o Sodium	hloride (NoCl)	47	
Cryolite	$(Na_3AlF_6)$	35	
Aluminu	n fluoride (AlF3)	12	

we have found to be highly satisfactory:

The salt bath has a melting point of about

Addition of a small amount of lithium chloride to the above composition lowers the melting point thereof. For example, addition of about For example, addition of about 20% lithium chloride lowers the melting point to about 1075° F.

The exact composition of the salt bath is not critical and the proportions of potassium chloride, sodium chloride, cryolite and aluminum fluoride may be varied from the above. For ex-35 ample, the potassium chloride may range from about 37 to 57%, the sodium chloride from about 25 to 45%, the cryolite from about 8 to 20% and the aluminum fluoride from about 0.5 to 12%. The bath composition usually preferred is one that will become molten when heated to  $1200^{\circ}$  F. or somewhat lower. While in the foregoing examples the double salt Na3AlF6 (cryolite) is given it should be understood that an equivalent amount of this component may be supplied in the form of the single salts, sodium fluoride and aluminum fluoride. We have found that it is essential to provide an excess of AlF3 over that of the cryolite ratio in order to obtain the desired results.

The temperature of the fused salt bath is maintained during operation at a temperature within the approximate range of 1250° to 1600° F. In general a temperature of 1300 to 1400° F. is preferred.

The molten metal coating bath may be pure

aluminum or an aluminum base alloy. In general the aluminum base alloys contain about 80% or more of aluminum. One aluminum base alloy that is particularly advantageous is one composed of about 5 to 15% silicon and the balance 5 aluminum. This alloy has a relatively low melting temperature, i. e. eutectic at 12% silicon and has high fluidity, both of these properties being highly advantageous in forming relatively non-brittle coatings. Effective drainage of excess 10 coating metal is obtained because of the high fluidity. Specific examples of other aluminum base alloys are the following: an alloy composed of 4% copper and the balance aluminum, an alloy composed of about 7% tin and 93% aluminum, 15 and alloys containing 5 to 20% zinc and the balance aluminum. These specific examples are referred to merely for purpose of illustration and not of limitation.

At present it is preferred that the temperature 20 of the aluminum or aluminum base alloy coating bath be maintained at a temperature of about 1250°-1325° F. Temperatures of about 1150° F. to about 1600° F. are suitable, however, for the aluminum base alloys. Pure aluminum melts 25 at about 1218° F. Consequently in employing pure aluminum as the coating metal a temperature of at least 1218° F. must be used. The upper temperature employed with pure aluminum as the coating metal is also about 1600° F.

After passing through the fused salt flux and into the molten aluminum or aluminum base alloy bath the coated steel or other ferrous metal emerges from the coating bath through the molten salt layer. There is a tendency to form a 35 thicker or heavier coating of aluminum or aluminum alloy than desired. By passing the coated ferrous metal slowly through the molten salt on emerging excess molten coating metal is drained off, or the coated ferrous metal may be 40 coating metal bath. We have found that the held in the fused salt after removal from the coating bath whereby excess coating metal may drain off. The coated ferrous metal after removal, or as it is being removed from the aluminum or aluminum alloy bath, may be vibrated rapidly or treated in other equivalent manner (rotate rapidly for example), in order to remove excess molten or mushy coating metal. Excess coating metal also may be removed by an air blast.

The coated steel or other ferrous metal is then cooled or allowed to cool. The excess flux may be removed as by washing, for example or the coated ferrous metal may be passed through rollers to remove the flux and to provide a desirable finish to the coated product. Water or other quenching mediums may be employed to cool the coated ferrous metal.

The steps of degreasing, pickling and immersing in the zinc chloride type of flux are not es-60 sential to the process, as the step of heating in the described fused salt prior to immersing in the aluminum or aluminum alloy bath will provide a clean surface on the ferrous metal unless it is exceptionally contaminated to begin with. 65

The steel or ferrous metal may be, if desired, preheated before being immersed in the fused salt bath. This permits smaller quantities of salt and smaller sized salt bath heating means. If the preheating step is employed, it is preferred 70 to heat the metal to be coated under such conditions that the surface thereof is not oxidized. For this purpose heating in a non-oxidizing or reducing atmosphere furnace such as one employing hydrogen, Drycolene, etc. may be employed. 75 aluminum or aluminum base alloy coating bath

The preheating temperature preferably is within the range of 1200° to 1600° F.

When the steel or other ferrous metal is preheated to the temperature of the fused salt bath in a reducing temperature and is free of oxides of iron and other foreign matter, the time of immersion in the fused salt bath may be as little as one or two seconds if the parts are free of complicated recesses. More complicated shapes may require a longer time in order to ensure that the fused salt thoroughly cover or coat the parts to be coated with aluminum or aluminum alloy. Where the steel or other ferrous metal has iron oxides on the surface thereof longer times will be required in order to provide clean steel surfaces. When the preheating step is not employed, suffcient time is required to bring the steel or other ferrous metal to a temperature at least as high as, and preferably somewhat above, the melting point of aluminum or the aluminum base alloy to be employed as the coating material. The time will, of course, depend on the gage and dimensions of the ferrous metal and on the size and thermal efficiency of the salt bath. Holding the ferrous metal in the fused salt for extended periods is not harmful.

The time of immersion in the molten aluminum or aluminum base alloy bath may vary from as little as one or two seconds up to several minutes, depending somewhat on the degree of complica-30 tion of recesses, etc., in the part being processed. A relatively short period of immersion is desirable to prevent excessive formation of brittle ironaluminum alloys. Ordinarily, therefore, the ferrous metal being coated is held in the molten aluminum or aluminum alloy bath ten seconds or less.

If desired, separate containers and heating means may be employed for the salt bath and the fused salt bath must be activated by aluminum in or in contact with the fused salt in order to provide; effective fluxing action. Where the fused salt is on top of the molten aluminum or aluminum base alloy as described above, the proper 45 activity of the molten salt is obtained. Where a separate salt bath and a separate aluminum or aluminum base alloy coating bath are employed, it is essential to activate the fused salt. This may be done by employing an aluminum or aluminum 50 alloy coated container for the fused salt, or aluminum or aluminum alloy can be added to the salt. The aluminum or aluminum alloy may be added by immersing a bar or sheet of the metal in the fused salt bath. The bar or sheet soon melts and 55 goes to the bottom of the salt bath.

The procedures described above constitute preferred embodiments of processing in accordance with our invention. However, it is possible to obtain satisfactory coatings of aluminum or aluminum base alloy on ferrous metal by a departure from the conditions of the preferred embodiments. For example, it is possible to immerse the ferrous metal in a molten aluminum or aluminum base alloy bath on which is floating a relatively thin layer of a molten or fused salt bath of the composition described in connection with the preferred embodiments of the invention at a temperature within the range of 1250° to 1600° F. The cold ferrous metal in passing through the layer of activated molten salt flux will become coated with a layer of the flux which may solidify, but which will again become molten after sufficient time of contact with the molten

underneath the fused salt layer. A satisfactory coating of aluminum on ferrous metal can be obtained by this procedure. It is possible, also, to obtain a satisfactory coating of aluminum on ferrous metal by heating the ferrous metal in our activated fused salt bath until the ferrous metal is at a temperature above the melting point of aluminum and then allow the ferrous metal and coating of said sait thereon to cool to some temperature below the melting point of aluminum 10 or salt before immersion in the molten aluminum or aluminum base alloy coating bath, so long as the salt coating if allowed to solidify on the ferrous metal is not cracked or broken prior to immersion in the molten aluminum coating metal 15 bath and so long as the ferrous metal is permitted to remain in the molten aluminum or aluminum base alloy for a time and at a temperature sufficient to reheat the ferrous metal and salt coating to a temperature of about 1250° F. or 20 higher. It is possible, also, to obtain satisfactory coatings of aluminum or aluminum base alloy on ferrous metal by heating the steel or other ferrous metal in the molten salt bath described herein, maintained at a temperature below that 25 of the molten aluminum or aluminum base alloy and, while the salt coating on the ferrous metal is still molten, immersing the ferrous metal and salt coating in a molten aluminum or aluminum base alloy coating bath and heating the same to a 30 temperature within the range of about 1250° to 1600° F.

Various changes and modifications of the embodiments of our invention described herein may be made by those skilled in the art without de- 35 parting from the principles and spirit of the invention.

We claim ·

1. A method of coating ferrous metal with a coating metal of the class consisting of aluminum 40 and aluminum base alloys which comprises immersing the ferrous metal in a fused salt bath composed about as follows:

> 37 to 57%, KCl 25 to 45%, NaCl 8 to 20%, Na<sub>3</sub>AlF<sub>6</sub> 0.5 to 12%, AlF3

said fused salt bath being activated by aluminum in contact with the fused salt, said fused salt bath 50 being at a temperature within the range of about 1250° F. to 1600° F., said ferrous metal having a temperature at least as high as the melting point of the said coating metal while in said activated salt bath, then immersing the ferrous metal in 55 a molten bath of said coating metal while the ferrous metal is at a temperature at least as high as the melting point of said metal coating bath and thereafter removing the coated ferrous metal from said metal coating bath.

2. A method as in claim 1 in which the ferrous metal is preheated to substantially the temperature of the salt bath before being immersed therein

3. A method as in claim 1 in which the ferrous 65 metal is immersed in the fused salt bath while the ferrous metal is at room temperature and is heated in the fused salt to a temperature at least as high as the melting point of said coating metal.

4. A method as in claim 1 which includes the 70 step of removing excess coating metal from the ferrous metal after removal from the coating bath and before the coating metal on the ferrous metal has completely solidified.

a coating metal of the class consisting of aluminum and aluminum base alloys which comprises immersing the ferrous metal in a fused salt bath composed approximately as follows:

37	to	57%	, KCl	
25	to	45%	, NaCl	Ċ
8 t	io 2	0%,	Na <sub>3</sub> AlF	8
0.5	i to	12%	, AlF <sub>3</sub>	-

said fused salt bath being at a temperature within the range of about 1250° to 1600° F. and floating on top of a molten bath of said coating metal immersing the ferrous metal in the molten coating metal bath while the ferrous metal is at a temperature at least as high as the melting point of said coating metal, and removing the coated ferrous metal through the said fused salt.

6. A method of coating ferrous metal with a coating metal of the class consisting of aluminum and aluminum base alloys which comprises immersing the ferrous metal in a fused salt bath composed approximately as follows:

47%,	KC1
35%,	NaCl
12%,	Na <sub>3</sub> AlF <sub>6</sub>
6%. A	1F5

said fused salt being activated by aluminum in contact therewith, said fused salt being maintained at a temperature within the range of about 1250° F. to 1600° F., said ferrous metal having a temperature at least as high as the melting point of said coating metal while in said activated salt bath, then immersing the ferrous metal in a molten bath of said coating metal while the ferrous metal is at a temperature at least as high as the melting point of said coating metal, and thereafter removing the coated ferrous metal from said bath of molten coating metal bath.

7. A method as in claim 6 in which the ferrous metal is preheated in a non-oxidizing atmosphere to substantially the temperature of the salt bath before being immersed therein.

8. A method as in claim 6 in which the ferrous 45 metal is immersed in the fused salt bath while the ferrous metal is at room temperature and is heated in said fused salt bath until it is at a temperature at least as high as the melting point of said coating metal.

9. A method as in claim 6 which includes the step of removing excess coating metal from the ferrous metal after removal from the coating metal bath and before the coating on the ferrous metal has completely solidified.

10. A method as in claim 6 in which separate salt and coating baths are employed and the ferrous metal is heated from room temperature to a temperature at least as high as the melting point of said coating metal while in said fused 60 salt bath and is then quickly transferred to the coating bath.

11. A method of coating steel with a coating metal of the class consisting of aluminum and aluminum base alloys which comprises immersing the steel in a fused salt bath composed approximately as follows:

47%,	KCI
35%,	NaCl
12%,	Na <sub>3</sub> AlF <sub>6</sub>
6%	AIRL

said fused salt bath being at a temperature within the range of about 1250° to 1600° F. and floating on top of a molten bath of said coating metal, 5. The method of coating ferrous metal with 75 lowering the steel into said coating metal bath

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while the steel is at a temperature at least as high as the melting point of said coating metal, and removing the treated steel through the said fused salt.

12. A method of coating steel with a coating s metal of the class consisting of aluminum and aluminum base alloys which comprises heating the steel in a fused salt bath composed approximately as follows:

> 47%, KCl 35%, NaCl 12%, Na3AlF6 6%, AlF3

said salt bath being at a temperature within 15 the range of about  $1300^{\circ}$  F. to  $1400^{\circ}$  F., said fused salt bath being activated by aluminum in contact therewith, the steel being heated to a temperature at least as high as the melting point of said coating metal while in said fused salt bath, then 20 immersing the heated steel in a bath of said coating metal heated within the range of about  $1250^{\circ}$  F. to  $1325^{\circ}$  F. for a time within the range of one to about ten seconds, and then removing the coated steel from the molten metal bath. 25

13. A method as in claim 12 which includes the step of removing excess coating metal from the steel after removal of the steel from the coating metal bath and before the coating on the steel has completely solidified, thereby forming 30 a relatively thin coating on the steel.

14. The method of treating ferrous metal preparatory to coating the same with a metal of the class consisting of aluminum and aluminum base alloys which includes immersing the ferrous 35 metal in a molten salt bath composed substantially as follows:

37	to	57%,	KCl
25	to	45%,	NaCl
8	to	20%,	Na3AlF6
).5	to	12%.	AlF <sub>3</sub>

said molten salt bath being maintained at a temperature within the range of about 1250°-1600° 8

F. while the ferrous metal is immersed therein, said molten salt bath having aluminum in contact therewith.

15. A method as in claim 11 in which the fused salt bath is at a temperature of approximately  $1300^{\circ}$  F. to  $1400^{\circ}$  F.

16. A method as in claim 11 which includes the step of removing excess coating metal from the steel after removal of the steel from the coating

10 metal bath and before the coating on the steel has solidified, thereby forming a relatively thin coating on the steel.

17. The method of coating ferrous metal with a coating metal of the class consisting of aluminum and aluminum base alloys which comprises passing ferrous metal into and out of said coating metal bath through a molten salt bath floating on said molten coating metal bath, said molten salt bath consisting essentially as follows:

> 37 to 57%, KCl 25 to 45%, NaCl 8 to 20%, Na3AlF6 0.5 to 12%, AlF3

25 said molten salt bath being maintained at a temperature of about 1250°-1600° F. while the ferrous metal is passing therethrough.

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