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METHOD OF COATING METALLIC BODIES WITH ALUMINUM  
UTILIZING VAPOROUS SUB-CHLORIDES  
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Fig. 1

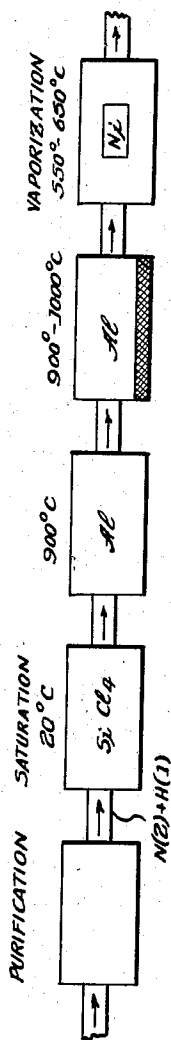
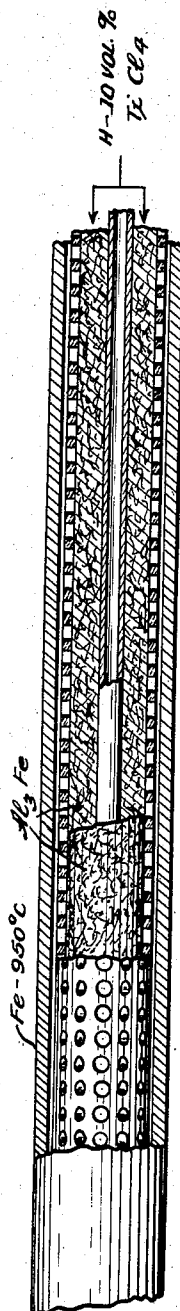


Fig. 2



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## METHOD OF COATING METALLIC BODIES WITH ALUMINUM UTILIZING VAPOROUS SUB-CHLORIDES

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2 Claims. (Cl. 117—107)

This invention relates to a method of coating metallic bodies with aluminum.

It is known that coatings of aluminum or aluminum alloys by treating a base metal with vapors of aluminum chlorides may be produced at elevated temperatures in an atmosphere free of oxygen and water vapors. The volatile aluminum chlorides are produced either by vaporizing sublimated  $AlCl_3$  or by chlorination of aluminum or aluminum-containing combinations in contact with chloride or hydrogenchloride or chloride-yielding chlorides such as ammonium chloride.

It has however been discovered that in such treatment, the base metal is strongly and detrimentally attacked by the chloride. Also, the appearance of a low-grade aluminum chloride (aluminum-subchloride) has under predetermined conditions been observed. The subchloride is formed by a reaction of  $AlCl_3$  vapor with molten aluminum. For technical processes, the use of the solid, moisture-sensitive aluminum chloride is however connected with great difficulties, for example, in the dosing or in its continuous vaporization in a stream of a carrier gas. Great difficulties also appear in the technical handling of the known analogously produced aluminum subchloride.

The invention proposes a method of producing upon metallic bodies aluminum coatings or aluminum alloy coatings. The alloy coatings thus produced may be formed as surface layers just as the aluminum coatings. With sufficiently long treatment of the base metal, for example, powdered base metal, it will be possible to obtain the penetrating reaction thereof into the desired aluminum alloy. In the method according to the invention, the formation of the aluminum alloys or vapor layers of aluminum is effected by treating the surface of the solid base metal with vaporous preferably low-grade aluminum subchlorides obtained directly prior to the vapor reaction from other vaporous metallic chlorides (foreign metallic chlorides) by reaction with aluminum or aluminum alloys, respectively.

Based upon thermodynamic data of aluminum chlorides, a reaction with nobler base metals could not be expected at all or only with very low yield. It was, however, found that the aluminum subchlorides formed according to the invention, exhibit extremely active reaction, being easily reacted with the corresponding base metals without attacking them by increased formation of chloride. This surprising effect is believed to be due to catalytic decomposition of the subchlorides through the metal surface without causing appearance of free chloride.

It has been found that aluminum subchlorides especially adapted for quick reaction with the base metal, are produced when the formation thereof by reaction of the foreign metal chlorides with aluminum or aluminum alloys takes place at temperatures within a range from above  $500^\circ C.$  to above  $900^\circ C.$ , exceeding the reaction temperature with the base metal (vaporization tempera-

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ture), and when the formed vaporous aluminum subchlorides do not go through an intermediate cooling, between their formation and the reaction with the base metal.

By the forming of the aluminum subchlorides according to the invention, substantially all metallic chlorides are adapted which assume vapor state at the formation temperature and which exhibit at such temperature a more negative value of the formation energy than that of the aluminum chloride. Accordingly, substantially only the alkali-chlorides and the earth alkalichlorides are unsuitable. It has, however, been found in practical work that accurate dosing of the aluminum subchloride in the carrier gas is of basic importance for obtaining uniform vapor reaction over the entire metallic surface to be treated. Such dosing may be achieved simply upon using foreign metal chlorides which are fluid or liquid at room temperature. Relatively inexpensive silicon tetrachloride which is liquid at room temperature has been found particularly suitable. Titanium tetrachloride may also be used with advantage provided that attention is paid to an atmosphere free of oxygen and water and also free of nitrogen.

Practical work will be in most cases carried on with an inert or a reducing carrier gas stream which is loaded with the vaporous foreign metal chlorides, for example, by saturation at predetermined temperature or by feeding liquid foreign metal chloride in drops to the carrier gas, and conducting such carrier gas stream for the reaction over or through the fluid aluminum and conducting the aluminum subchlorides formed in such carrier gas stream to the metal surface to be coated.

The method of the invention is excellently adapted for providing iron and alloyed steels with coatings or layers of aluminum alloys; for the forming of such coatings upon nickel and chromium-nickel alloys; for aluminizing molybdenum and its alloys; for producing chromium-aluminum alloys, etc. Aluminum, iron-aluminum or nickel-aluminum and other alloys are adapted for yielding the aluminum in the reaction with the foreign metal chlorides.

The invention will now be described by explaining a few examples:

### Example 1

A gaseous stream, freed of oxygen and water, of 2 parts nitrogen and 1 part hydrogen, by volume, is saturated with silicon tetrachloride at  $20^\circ C.$  The resulting gas mixture containing about 20 vol.-percent  $SiCl_4$  is forced through an aluminum bath held at  $900^\circ C.$  and is then conducted over liquid aluminum ( $900^\circ-1000^\circ C.$ ) to the vaporization furnace, the latter containing a body of nickel which is to be aluminized, such body being held at a temperature from  $550^\circ-650^\circ C.$  A treatment of about 40 min. will produce a uniform aluminum silicon alloy coating about 0.02 to 0.05 mm. thick. See Fig. 1.

### Example 2

Iron pipes may be treated to provide aluminum alloy coatings or layers on the inside as diagrammatically indicated in Fig. 2. A perforated ceramic carrier tube is introduced into the iron pipe, with a few millimeters clearance. The tube has concentrically disposed therein a thin ceramic heating tube, the space between the heating tube and the carrier tube being filled with powdered ferroaluminum, for example,  $Al_3Fe$ . Along the heating tube is concentrically conducted hydrogen carrier gas with 10 vol.-percent  $TiCl_4$ . The heating tube is kept at  $1150^\circ-1200^\circ C.$  and heats the ferroaluminum filling with a corresponding temperature drop to the outside temperature of the pipe which is by outside heating held at  $950^\circ C.$  The reaction gas which contains the aluminum

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subchloride formed according to the invention penetrates the perforated carrier tube, flows to the inside pipe wall and is exhausted at one end of the pipe. An aluminum-titanium alloy coating with a thickness on the order of about 0.1 to 0.2 mm. may be produced by a treatment lasting from about 20 to about 30 min. Such interiorly coated pipes are proof against burning out in oxygen and water vapor up to about 1000° C. without cracking of the coating. The interior treatment described above may be advantageously combined with known diffusion annealing on the outside of the pipe. For example, by using sprayed aluminum coatings with silicate cover layers, the outer annealing may be carried out without protective gas while the interior protective gas treatment according to the invention may be simply accomplished by sealing the pipe at its ends.

#### Example 3

Molybdenum powder is converted to molybdenum-aluminate powder, in a flowing bed, by treatment with a gas stream containing aluminum-chloride-hydrogen at 1200° C. The production of the aluminum chloride is according to the invention accomplished by reaction of a mixture of  $\text{SiCl}_4\text{-H}_2$  at 1250°-1300° C. with an aluminum melt. The conversion of the molybdenum powder into molybdenumaluminate is accomplished in a few minutes. This example has not been illustrated because it is believed self-explanatory in view of the preceding description.

Changes may be made within the scope and spirit of the appended claims.

I claim:

1. A method of coating metallic bodies with aluminum alloys, comprising the following steps, namely, reacting with aluminum, at temperatures within the range from

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above 500° C. to above 900° C., metallic chloride selected from the class of chlorides consisting of silicon tetrachloride and titanium tetrachloride contained in a hydrogen carrier gas, to produce low grade vaporous aluminum subchloride and silicon subchlorides or titanium subchlorides, respectively; and conducting said low grade subchlorides directly upon formation thereof, with said carrier gas, to a metallic body to be coated, for interaction with said body at a temperature which is below the temperature at which said subchlorides are formed, to cause deposit on said metallic body of an aluminum alloy coating.

2. A method of coating metallic bodies with aluminum, comprising the following steps, namely, reacting with aluminum, at temperatures within the range from above 500° C. to above 900° C., metallic chloride which is liquid at room temperature and selected from the class of chlorides consisting of silicon tetrachloride and titanium tetrachloride contained in a hydrogen carrier gas, to produce low grade vaporous aluminum subchloride, and conducting said low grade aluminum subchloride directly upon formation thereof, with said carrier gas, to a metallic body to be coated, for interaction with said body at a temperature which is below the temperature at which said aluminum subchloride is formed, to cause deposit on said metallic body of an aluminum alloy coating.

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