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2,988,465

**METHOD OF PRODUCING CHEMICAL CONVERSION COATINGS ON ALUMINUM SURFACES**

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No Drawing. Filed Nov. 19, 1959, Ser. No. 854,005  
5 Claims. (Cl. 148-6.2)

This invention relates to the art of producing chemical conversion coatings on the surface of aluminum or alloys thereof in which aluminum is the principal or predominant ingredient and is primarily concerned with aluminum coating processes in which the surface of the metal is treated with acidic solutions containing fluorine bearing compounds and hexavalent chromium. The invention is particularly useful in the treatment of large areas of aluminum surface in relatively short periods of time and particularly under conditions of heavy bath loading, i.e., where large surface areas are treated per unit volume of bath per unit of time.

In situations of this kind it is most important that the bath or solution which is used in the process be kept in proper operating condition and the present invention has for its primary object the provision of certain improvements in the replenishing technique whereby the bath may be maintained in suitable condition for the rapid production of useful and uniform coatings both as to color and corrosion resistance even in situations where the bath is being subjected to heavy loading.

The nature and advantages of the invention will be better understood if certain prior art practices are kept in mind. For instance, it is well known that highly corrosion-resistant as well as decorative coatings can be produced on aluminum surfaces by treating them with acidic solutions containing fluorine bearing compounds and hexavalent chromium as their principal and essential ingredients. (It should be noted at this point that in the present disclosure wherever the term "fluorine bearing compound" appears it is used to mean any compound containing an atom of fluorine in its makeup whether or not the fluorine present is in the form of a simple or complex fluoride.) It is also well known that coatings produced by solutions of this type can be further improved by including in the solutions, as an addition agent, some ferricyanide. As a general rule the art, as presently practiced, has involved replenishment of the coating solutions with the same concentrates as were employed in making up the original bath. Additionally, in replenishing such solutions, it has been customary, if necessary, to add from time to time sufficient mineral acid such as nitric acid to maintain the coating solution at the desired degree of acidity.

Unfortunately, the foregoing practices of the prior art have not always been successful in maintaining the ability of the coating bath to produce the desired degree of uniformity in coating, especially in processes which involve the treatment of large areas of aluminum in relatively short periods of time. This problem has been experienced to a marked degree in strip line production where the coating baths are subjected to unusually heavy loading.

The compositions of coating solutions of the character described are well known in the art, and by way of example reference may be had to United States Patents 2,276,353; 2,507,956; 2,851,385; 2,796,370 and 2,796,371. It will be noted from the last two patents listed that the presence of ferro or ferricyanide ions in the bath significantly improves the coating characteristics of a bath which consists principally and essentially of fluor-

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ine bearing compounds and hexavalent chromium. Industrially, baths of the type described have become extremely important and there are a number of materials commercially available by means of which the solutions may be initially prepared and subsequently replenished. Examples of these which are well known to the trade are sold under the trademarks "Alodine," "Iridite" and "Bonderite." The Alodine solutions for this purpose are known as Alodine 600 and Alodine 1200, the Iridite is known as Iridite 14 and Iridite 14-2 and the Bonderite is known as Bonderite 721, and all of these consist primarily and essentially of hexavalent chromium, a fluorine bearing compound containing either a simple or a complex salt, and a cyanide selected from the class consisting of ferro and ferricyanides, together with mineral acids as may be necessary to produce the desired range of pH in the coating bath.

The practices of the art to which reference has been made have quite often resulted in the production of coatings which are non-uniform in both appearance and corrosion resistance, especially where the coating solutions are employed in the treatment of a long succession of aluminum surfaces in relatively short periods of time.

The present invention overcomes the previous difficulties and is based upon the discovery that, if coating solutions of the type described are replenished from time to time by restoring the hexavalent chromium content to the desired level and, further, that if the fluoride and the ferricyanide are added to the bath in a definite relationship to the amount of hexavalent chromium that is added, it is possible to maintain the bath in such condition that it will produce uniformly colored and corrosion resistant coatings even in situations where a long succession of aluminum surfaces are treated over relatively short periods of time. Furthermore, in replenishing the fluoride content, we have found that it is necessary to employ a simple fluoride regardless of whether or not the bath was originally made up or formulated with complex or simple fluorides. Specifically, in the present invention, the fluoride which is added to the bath must be added in the form of hydrofluoric acid or an alkali or ammonium salt of such acid and the addition must be made in a quantity from 0.4 to 2 parts of the fluoride in the form just mentioned for each part of chromate added (calculated as  $\text{CrO}_3$ ).

When the source of fluoride is hydrofluoric acid, best results are secured by adding between 0.5 and 0.75 part of fluoride for each part of chromate. In general, if hydrofluoric acid is the source of the fluoride, not more than .8 part F should be added for each part of hexavalent chromium. Furthermore, where the fluoride is introduced by additions of alkali or ammonium salts, best results are secured by adding 0.75 part to 1.25 parts of salt for each part of chromate added. If less than 0.5 part fluoride is added for each part of hexavalent chromium (calculated as  $\text{CrO}_3$ ) it will be noted that the uniformity of the coatings produced by the bath will be rapidly impaired or no visible coatings whatsoever will be produced. When the amount of fluoride added is more than 1 to 2 parts for every part of hexavalent chromium added, the color of the coating gradually becomes lighter and lighter until no visible coating is produced.

In situations where rather brilliant colors are desired in the coating the bath should also contain ferricyanide and in replenishing this ingredient there should be added at least 0.05 part of ferricyanide and preferably from 0.2 to 1 part of ferricyanide for each part of chromate which is added to the bath. When less than 0.05 part of ferricyanide is added the color imparted to the coating will, over a given period of time, become lighter and lighter and the coating weight will gradually diminish.

Although we have just indicated a maximum of 1 part as a potential upper limit on the quantity of ferricyanide added we wish to say that such limit is dictated by reasons of economy rather than by necessity because the use of more than 1 part does not seem to harm the process or the results attained in any way.

Obviously, it is essential that the acidity of the invention be controlled. This may be done in whole or in part by replenishment of the hexavalent chromium content as chromic acid and of the fluorine content as hydrofluoric acid or a simple salt thereof. As a general practice the preferred method of controlling the bath pH is through the use of chromic acid ( $\text{CrO}_3$ ) and hydrofluoric acid, but in situations where this is not effective an amount of mineral acid, preferably nitric acid, may be added as needed to maintain the desired degree of acidity.

Solutions replenished in accordance with the foregoing instructions are capable of coating large areas of aluminum surfaces with a remarkable degree of uniformity both as to color and corrosion resistance and this in relatively short periods of time during a continuous operation. As an actual matter of fact, coating baths, replenished as described, have been in substantially continuous operation under conditions of extremely heavy bath loading in the coating of literally millions of square feet of aluminum and the coatings produced have been of remarkably uniform quality throughout both as to color and corrosion resistance.

We will now cite some specific examples. Utilizing commercially available materials a bath was prepared in accordance with the practices of the prior art and the resulting solution had the following composition which, for the sake of convenience, we will refer to as

#### Experiment I

	Grams
Chromic acid ( $\text{CrO}_3$ )	4.5
Sodium fluoborate ( $\text{NaBF}_4$ )	6.0
Potassium fluozirconate ( $\text{K}_2\text{ZrF}_6$ )	1.65
Potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ )	2.85
Water, to make 1 liter.	

The foregoing bath, as initially prepared, had a pH of 1.5 and was used to coat 3S aluminum alloy pieces utilizing a 1-minute immersion time at room temperature. The bath produced strongly corrosion resistant coatings having a beautiful golden brown color. Subsequently, a series of aluminum coils was processed in rapid succession through this bath also at room temperature until a total of 40 ft.<sup>2</sup> of aluminum surface had been coated. The coating solution was analyzed and replenishment was effected after every 10 square feet of aluminum had been coated and this replenishment was carried out in accordance with the manufacturer's directions and the practices of the prior art and at the same time the pH was adjusted with suitable additions of nitric acid to maintain the same at substantially its original value. However, by the time that the 40 ft.<sup>2</sup> of aluminum surface had been processed and even after only four replenishments, the coatings produced by the bath had greatly diminished in color intensity and were obviously inferior to the coatings produced by the bath as originally prepared.

To contrast the foregoing with the improvements of the present invention another bath was prepared of identical composition to the one given above which bath initially, and under the same conditions as noted above, produced strongly colored golden brown coatings. However, this bath was replenished in accordance with the teachings of the invention herein disclosed. Specifically, for every 10 ft.<sup>2</sup> of surface coated the bath was restored to its original hexavalent chromium content and at the same time, for each part of chromate added, there was added 0.5 part of fluoride in the form of hydrofluoric

acid and 0.6 part of ferricyanide. When necessary the acidity of the bath was adjusted to its original value with suitable additions of nitric acid. When the bath was handled in this way it produced uniformly colored coatings even after 100 ft.<sup>2</sup> of aluminum surface per liter of bath volume had been processed. In fact, the coating produced on the hundredth square foot was practically identical with the coating first produced by the bath.

In the comparison just noted, coating weight determinations were made and when the operation was carried out according to the practices of the prior art, after processing 40 ft.<sup>2</sup>, it was found that the fortieth square foot of surface had a coating weight which was approximately 23% less than the coating weight originally produced by the bath, whereas, when operating according to the method of the present disclosure, the coating weight on the hundredth square foot was practically identical to the coating weight produced on the first square foot.

Still further examples of the process of the present invention are found in the following:

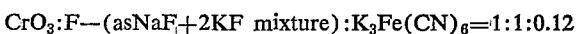
#### Experiment II

An aluminum coating bath was prepared containing the following constituents:

	Grams
Chromic acid ( $\text{CrO}_3$ )	5
Potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ )	0.60
Hydrofluoric acid (HF)	1.05
Water, to make 1 liter.	

This bath, as initially prepared had a pH of 1.5 and was used to coat 3S aluminum alloy panels using a 1-minute immersion cycle at room temperature. Panels treated initially were uniformly golden brown in color and had coating weights of 80 mg./ft.<sup>2</sup>.

A series of aluminum coils was subsequently processed in rapid succession through this bath at room temperature until a total of 100 ft.<sup>2</sup> of aluminum surface area had been coated. The coating solution was analyzed and replenished every 20 sq. ft. with  $\text{CrO}_3$ , a mixture of NaF and KF in the molar ratio of 2 parts K to 1 part Na and  $\text{K}_3\text{Fe}(\text{CN})_6$ . The ratios of the replenishing materials were:



The pH was adjusted to the desired 1.5 to 1.7 range using small increments of concentrated nitric acid. Aluminum panels coated for 1 minute in this bath, replenished in the above manner, were found to be quite consistent in color uniformity. Coating weights from start to finish, as well as color, were substantially uniform.

#### Experiment III

An aluminum coating bath was prepared containing the following constituents:

	Grams
Chromic acid ( $\text{CrO}_3$ )	5.0
Potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ )	0.6
Hydrofluoric acid (HF)	1.05
Water, to make 1 liter.	

This bath, as initially prepared had a pH of 1.5 and was used to coat 3S aluminum panels using a 1-minute immersion cycle at room temperature. Panels treated initially were uniformly golden brown in color and had coating weights of approximately 80 mg./ft.<sup>2</sup>.

A series of aluminum coils was subsequently processed in rapid succession through this bath at room temperature until a total of 100 ft.<sup>2</sup> of aluminum surface area had been coated. Analysis was made of the coating solution and replenished every 20 sq. ft. with  $\text{CrO}_3$ , F (as HF) and  $\text{K}_3\text{Fe}(\text{CN})_6$  in the ratio of 1:0.5:0.12 by weight. No nitric acid was added during this run since the pH was found to have remained constant. The final pH was 1.5. Aluminum panels coated for one

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minute in this bath replenished in the above manner were found to have remained quite constant in color uniformity.

We claim:

1. In the production of chemical conversion coatings on a succession of aluminum surfaces where the surface is treated with an aqueous acid solution consisting essentially of a fluorine bearing compound and hexavalent chromium, the method of maintaining the solution in coating condition throughout its operating life which comprises periodically restoring the hexavalent chromium content of the solution to the desired level and replenishing fluorine by adding fluoride from the class consisting of hydrofluoric acid and alkali and ammonium salts thereof, the quantity of fluoride from said class which is added being from 0.4 to 2 parts for each part of chromate (calculated as CrO<sub>3</sub>).

2. The method of claim 1 wherein the fluoride is added as hydrofluoric acid in an amount of from 0.5 to 0.8 part for every part of chromate added.

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3. The method of claim 1 wherein the fluoride is added as salt from the said class in an amount of from 0.75 part to 1.25 parts for each part chromate added.

4. The method of claim 1 wherein the solution also contains ferricyanide as an addition agent and wherein said agent is replenished by adding from 0.05 to 1 part thereof for each part of chromate added.

5. The method of claim 1 wherein the solution also contains ferricyanide as an addition agent and wherein said agent is replenished by adding from 0.2 to 1 part thereof for each part of chromate added.

References Cited in the file of this patent

UNITED STATES PATENTS

2,507,956	Bruno et al. -----	May 16, 1950
2,796,371	Ostrander et al. -----	June 18, 1957
2,825,697	Carroll et al. -----	Mar. 4, 1958

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