

[54] **METHOD OF ELECTRODEPOSITING
ONTO STAINLESS STEEL**

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[56] **References Cited**

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[57] **ABSTRACT**

A process by which a metal may be plated on a stainless steel metal substrate whereby the final electro-plated composite possesses greatly improved adherence. Said process involves the electrodeposition of a chromium strike layer on the stainless steel base metal which is then followed by a nickel strike layer prior to plating of said metal. The chromium strike layer may be deposited from any standard chromium electrodeposition plating baths. The nickel strike layer may be deposited from a "Woods strike" nickel electroplating bath which can be either bromide or chloride. The bromide type is preferred and the composition and operating conditions of said bath comprise:

NiBr ₂	100-800 g./l.
HBr	0.2-20% by weight
Current Density	5-200 a.s.f.
Bath temperature	60-115° F.

4 Claims, No Drawings

METHOD OF ELECTRODEPOSITING ONTO STAINLESS STEEL

The instant invention relates to a process and metal composite formed thereby, whereby various metals may be adherently applied to a stainless steel substrate.

The invention further relates to the electrodeposition of a nickel strike from a chloride or bromide type "Woods strike" over a chromium strike which has been directly electrodeposited on the stainless steel substrate prior to deposition of said metal which is desired to be firmly adhered to the stainless steel substrate.

The use of stainless steels as substrates under other electrodeposited metals is not new to the art but such has achieved only limited application in various industries due to the fact that it is particularly difficult to secure adequate adhesion to the stainless steel substrate. Stainless steels themselves vary greatly in the degree of adherence that can be obtained through electrodeposited coatings. The instant invention as indicated previously, greatly improves the adherence of numerous metals wished to be deposited on stainless steels in general. However, the present invention has its greatest applicability when used in conjunction with the stainless steels on which it is more difficult to deposit an adherent coating.

The present invention will be described in more detail with respect to a particular stainless steel, namely, type 446 stainless steel although it is equally applicable to other deposit of stainless steel.

In the manufacture of Geiger Mueller radiation detector tubes, it is desirable to adhere on the internal surface of the stainless steel body of said radiation detector tube a metal deposited which is inert to the corrosive gases contained therein. It has been attempted in the past to electroplate platinum or other metal on the internal walls of such stainless steel tubes. Such attempts to electroplate platinum directly onto the inner surface of such stainless steel tubes were unsuccessful in view of poor adhesion on the platinum. Numerous pre-treatments were tried on the stainless steel surface prior to deposition of the platinum with little success. Utilizing some complex pre-treatments of the stainless steel, however, would result in some success, but the rejection rate of such tubes due to non-adherence of platinum or other noble metal clearly pointed out the commercial unfeasibility of such a process.

Adequate adherence by the adjacent metal layers is of course, dependent on the intermetallic bond established by said materials. The strength of the intermetallic bond required will, of course, depend on the end use of the article and the conditions it must endure. The instant invention thus, is most beneficial when applied to articles which are subject to high temperature changes or those which must later undergo considerable forming or bending.

Likewise, the surface condition of this stainless steel substrate is also extremely important. Whether the substrate has been rolled, heat treated, annealed, etched or been subject to various cleaning cycles or other pre-treatment, the practice of the present invention produces a more adherent metal layer due to the intermediate chromium strike and nickel strike when compared to directly applying said metal layer to said stainless steel substrate.

The theory behind the instant invention is to apply intermediate metallic layers which of themselves are highly adherent to the metal on which they are deposited, the chromium layer being highly adherent to the stainless steel substrate and the nickel strike being highly adherent to the underlying chromium strike while the final metallic layer is highly adherent to said nickel strike layer. In this manner the finished metallic composite of greatly improved adhesion is attained which can successfully withstand great variation in temperature as well as physical distortion such as is caused by bending or the like.

The metal layer which is desired to be adherently attached to the stainless steel substrate through the intermediate nickel and chromium strike layers of the instant invention can be any of numerous metals, for example, brass, bronze, cadmium,

copper, gold, indium, iridium, nickel, palladium, platinum, rhodium, silver, tin or zinc. Likewise, more than one metallic electroplate may be utilized over said intermediate nickel strike layer which effects the intermetallic bond with the stainless steel which results in the improved adherence contemplated by the instant invention.

As stated earlier, such intermediate metallic layers in the practice of the present invention are a chromium strike directly on the stainless steel substrate followed by a nickel strike. The chromium strike can be accomplished using any of the standard commercial processes for depositing chromium. In its broadest sense it need only consist of a chromic acid solution containing a catalyst. Such plating of chromium has been widely discussed in the literature see for example, the Metal Finishing Guide Book for 1967, pages 240-244 wherein typical chrome electroplating baths are discussed. The nickel strike of the present invention is accomplished from a Woods strike bath. The typical Woods strike bath is of the chloride type. Woods strike baths are well known to those skilled in the art of electroplated nickel. The use of such standard Woods strike baths, however, when applied directly to stainless steel, will not result in the improved adherence contemplated by the instant invention whether on the more easily plated stainless steels or in the case of the more difficultly plated stainless steels wherein such standard Woods strike baths produce only a deposit possessing inadequate adherence. However, the typical chloride type Woods strike when electroplated over a chromium strike produces a composite having the improved adherence required of the instant invention. The adherence can be further improved by utilizing a bromide type Woods strike rather than the standard chloride type.

A typical chloride type Woods strike nickel electroplating bath contains 32 oz. per gallon $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (240 g/l) and 16 fluid oz. per gallon HCl (12½ percent by weight). Such a nickel strike is deposited at room temperature under standard current density.

In general, we have found that stainless steels become more difficult to use as a substrate on which a strongly adherent metal electrodeposit is desired as the chromium content of the stainless steel increases. With certain high chromium content stainless steels and particularly with type 446 stainless steel, adherence of the nickel strike from a standard chloride Woods strike when applied directly to the stainless steel substrate was inadequate and could not be appreciably improved by varying the concentration of nickel chloride and/or HCl over wide ranges. During our experimentation in which tests were made in an attempt to improve the adherence of the standard chloride "Woods strike" to the stainless steel, it was found that even after various types of pre-treatments including several etchings, adequate adherence could not be obtained by using a standard Woods strike type bath in which the nickel chloride was between 150-300 g/l or more and the hydrochloric acid concentration filled from about 0.2-20 percent in the bath.

Such problem as described in the previous paragraph has been successfully solved and such solution is described in a co-pending application by the inventor hereof filed on even date herewith, namely, Ser. No. 70,559, filed Sept. 8, 1970. In this co-pending application, such standard Woods strike baths must be modified by replacing the nickel chloride and hydrochloric acid therein with nickel bromide and hydrobromic acid. The composition of such a bromide Woods strike bath may vary widely. The nickel bromide concentration can vary from approximately 100-800 g/l while the HBr content can vary from 0.2-20 percent by weight. The current density utilized in such a bath is generally in the range of 5-200 amps per sq. ft. and the plating time can be anything up to approximately 10 minutes although it is preferred to use as short as possible plating times. Preferably such baths are operated at room temperature, however, such may be operated up to a temperature of approximately 115° F.

It has been found that this bromide type Woods strike described in said co-pending application is likewise the

preferred bath to accomplish the nickel strike of the instant invention. However, in the instant invention the standard chloride type Woods strike can be utilized over the chromium strike layer to obtain a metal composite having improved adherence although such adherence is not as good as that obtained from a bromide type Woods strike over a chromium strike. The concentrations and operating conditions for the chloride type Woods strike are approximately the same as the bromide type Woods strike and in each case the preferred bath concentration for the Woods strike electroplate bath of the instant invention is a nickel bromide or nickel chloride concentration of approximately 500 g/l and a hydrobromic or hydrochloric acid concentration of approximately 0.4 percent by weight. Operation of said preferred bath would be at room temperature with a current density of approximately 16 amps per sq. foot for approximately 5 minutes.

To more fully describe the instant invention, a typical example is given hereinafter wherein a chromium strike is deposited directly on a type 446 stainless steel tube which is to be used in Geiger Mueller radiation detection devices after it is further plated with the nickel strike of the instant invention followed by a platinum electrodeposited final layer. Such a typical Geiger Mueller radiation detection device is fully described in U.S. Pat. No. 3,342,538 issued Sept. 19, 1967.

EXAMPLE

A stainless steel type 446 length of tubing having a wall thickness of 0.010 in. was first cathodically cleaned in a conventional alkaline cleaner at 180°-210° F for 15 seconds. After a cold water rinse the stainless steel tube was dipped for a few seconds with agitation in a 20 percent by volume hydrochloric acid solution and thereafter rerinsed. After the cleaning and rinsing operations, the tube was placed promptly in a typical commercial decorative chromium plating bath comprising 250 g/l CrO₃ and 2.5 g/l H₂SO₄ and plated at a current density of 50 amps per sq. ft. for 3 minutes. Thereafter the stainless steel tube with the chromium strike thereon was placed promptly in a nickel bromide electroplating bath and plated for 5 minutes at 16 amps per sq. ft. The bath composition was 500 g/l nickel bromide and 7½ milliliters per liter of

48 percent by weight solution of HBr. After removing and rinsing the nickel plated stainless steel tube, it was electroplated with platinum from a conventional platinum plating bath. The platinum bath was made up as follows:

Ammonium nitrate	13 oz.
Sodium nitrate	1.5 oz.
Platinum compound	10 g. (as Platinum)
Ammonium hydroxide	200 ml.
Water	1 gal.
Temperature	210° F.
Current density	60 a.s.f.

Adherence of all layers to the substrate was excellent as indicated by the fact that the metal composite could be given a 180° bend of short radius without separation of any of the intermetallic layers. In each of the plating cycles, the stainless steel tube acted as the cathode and the anode consisted of a centrally aligned wire running through the stainless steel tube.

- I claim:
1. A method of firmly adhering platinum to a stainless steel substrate comprising electrodepositing a chromium strike layer on said stainless steel substrate, thereafter electrodepositing a nickel strike over said chromium strike layer and subsequently electrodepositing said platinum onto said nickel strike layer, said nickel strike being electroplated from an aqueous nickel electroplating bath comprising 100 to 800 grams per liter nickel bromide or nickel chloride and 0.2 to 20 percent by weight hydrobromic or hydrochloric acid, said electrodeposition of said nickel strike being effected at a current density between 5 and 200 amps per square foot.
 2. The method according to claim 1 wherein the stainless steel substrate comprises a high chromium content stainless steel.
 3. The method according to claim 2 wherein the stainless steel substrate is tubular.
 4. The method of claim 1 wherein the nickel electroplating bath comprises approximately 500 g/l of nickel bromide or nickel chloride and approximately 0.4 percent by weight of hydrobromic or hydrochloric acid.

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