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CATHODIC ACTIVATION OF STAINLESS STEEL

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28 Claims

ABSTRACT OF THE DISCLOSURE

Processes for production of stainless steel articles such as, for example, stainless steel wires, strips, sheets and the like by activating the surface of a stainless steel substrate by cathodic treatment in an aqueous acid bath at high current density followed by electroplating the activated surface to provide the desired layer or layers of electroplate.

BACKGROUND OF THE INVENTION

The cleaning of stainless steel prior to electroplating involves a difficulty in that a thin, transparent and tenacious oxide film is present on the metal. This film has the property of reforming quickly on exposure to air or other oxidizing conditions even after it has once been removed. The presence of this film prevents adherent coatings of metals being applied by electroplating, and it is necessary to remove the film before electroplating. In view of the risk of rapid reforming of the oxide film, it is then usual to apply a first layer of the electroplated metal immediately after removal of the film and before the film can commence to reform, and subsequently to apply a second layer of the desired electroplated metal.

The removal of the oxide film from stainless steel prior to electroplating is generally termed "activation." Many methods have been proposed for the activation of stainless steel. Some such methods include cathodic or anodic treatments followed by immediate application of a protective so-called "strike" layer on to which the desired electroplated layer or layers can subsequently be applied. In other methods, the treatment is such that the oxide film is removed and a "strike" layer is simultaneously applied; this can for example be achieved by means of a cathodic treatment with certain nickel chloride/hydrochloric acid baths. In all these known methods, a strike layer which may for example be of nickel, zinc, cobalt or cadmium is applied to protect the stainless steel after removal of the oxide film and the desired electroplated layer or layers are subsequently applied. The strike layer is itself applied by electroplating, and thus at least two electroplating steps are involved.

SUMMARY OF THE INVENTION

The present invention is based upon the discovery that it is possible rapidly to activate stainless steel and to avoid the necessity of applying a strike layer by cathode treatment of the stainless steel in an aqueous acid bath at high current density.

According to the present invention there is provided a process for the production of an electroplated stainless steel article which comprises activating the surface of a stainless steel substrate by cathodic treatment in an aqueous acid bath at high current density, followed by electroplating the activated surface to provide the desired layer or layers of electroplate.

Following activation under such conditions, the desired electroplated layer or layers may be applied to the stainless steel without the need for application for an intermediate protective strike layer.

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The aqueous acid bath used for activation in accordance with the present invention may contain mineral acids such as for example H_2SO_4 , HCl , H_3PO_4 , HF , HF and NH_2SO_3H . The acid will advantageously be present in the bath in a concentration to provide a pH of less than about 4. The current density used during activation is preferably at least 10 a./dm.² and is advantageously from 10 to 300 a./dm.². The treatment is conveniently carried out using DC electricity with the stainless steel article to be coated as cathode and an anode of any conductive material which does not release metal ions into the bath.

The residence time of the stainless steel article to be coated in the bath is generally not critical and can vary within wide limits. The residence time may however, for example, be in the range of from 0.1 second to 1 minute, and the fact that such short residence times are possible makes the process according to the invention especially useful for the treatment of stainless steel articles such as wires, strips, sheets and the like. Such articles can with advantage be treated by continuous passage through an activating bath, the articles being activated on the run as they pass through the bath.

Following activation, the desired electroplated layer or layers can be applied to the stainless steel articles by any convenient method without application of an intermediate strike layer. Again with articles such as wires, strips, and sheets, the electroplating is with advantage effected during continuous passage of the article through an electroplating bath or baths. The electroplating baths may for example be aqueous acid baths, advantageously with a pH not greater than 5. Using such baths, electroplated layers of metals such as for example zinc, iron, cadmium, nickel, lead, manganese, copper, silver and gold can be applied. If desired, aqueous alkaline electroplating baths may also be used; copper and zinc are examples of metals which can conveniently be thus applied.

Additives such as for example brightening agents, may be incorporated into the electroplating baths as required.

Before activation in accordance with the present invention, the stainless steel may require cleaning. This is particularly so where the surface of the stainless steel article to be treated is very impure. Cleaning may thus for example comprise an anodic treatment in dilute aqueous solutions of hydrochloric, sulphuric or phosphoric acid. The current density and treatment time will depend upon the degree of impurity of the stainless steel surface. The more impure the surface, the more total current (i.e. current density x time) will in general be required to prepare the surface for cathodic activation in accordance with the invention. Current densities of from 1 to 100 a./dm.² and treatment times of from 0.1 second to 1 minute may for example be used with advantage. The anodic cleaning treatment may be combined with other cleaning treatments e.g. an initial simple immersion of the stainless steel article in aqueous acid or alkaline baths.

By the use of processes according to the invention, it is possible to apply on to stainless steel articles electroplated layers of metals which are of good quality and which are very firmly bonded to the stainless steel articles.

EXAMPLES

The following examples illustrate the invention:

EXAMPLE 1

A stainless steel wire, diameter 3 mm., is continuously passed into and through a bath containing an aqueous solution of 200 g./l. sulphuric acid. The wire is cathodically treated in the bath at a current density of 30 a./dm.² with

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a lead anode, the residence time of the wire in the bath being one second.

After withdrawal from the bath, the wire is fed into a second bath containing 200 g./l. $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ and 200 g./l. H_2SO_4 . The wire is cathodically treated in this second bath at a current density of 35 a./dm.². A copper coating of very good quality is thereby electroplated on to the stainless steel wire. This copper coating has very good adhesion to the stainless steel and no clefts occur when the wire is subsequently bent.

EXAMPLE 2

A stainless steel wire, diameter 3 mm., is passed continuously into and through a bath containing an aqueous solution of 150 g./l. phosphoric acid. The wire is cathodically treated in the bath at a current density of 20 a./dm.² with a carbon anode, the residence time of the wire in the bath being 0.5 second.

After withdrawal from the bath, the wire is fed into a second bath containing 100 g./l. $\text{Pb}(\text{BF}_4)$, 30 g./l. HBF_4 and 30 g./l. H_3BO_3 . The wire is anodically treated in this second bath at a current density of 10 a./dm.². The lead layer deposited is of very good quality and shows good adhesion to the stainless steel.

EXAMPLE 3

A stainless steel wire, diameter 3 mm., is passed continuously into and through an aqueous solution of 90 g./l. H_2SO_4 and 60 g./l. HCl . The wire is anodically treated in the bath at a current density of 10 a./dm.², the residence time of the wire in the bath being one second. The wire is subsequently subjected to a cathodic treatment followed by cathodic electroplating as described in Example 1 or Example 2.

EXAMPLE 4

Stainless steel wire is first immersed in an aqueous bath containing 100 g./l. of hydrochloric acid at a temperature of 50° C. for five seconds. The wire is next anodically treated in an aqueous bath containing 50 g./l. of sulphuric acid for three seconds at a current density of 20 a./dm.². The wire is next rinsed in water, and is then cathodically treated in an aqueous bath containing 150 g./l. of sulphuric acid for six seconds at a current density of 20 a./dm.². The wire is afterwards rinsed again with water and is finally electroplated in a bath containing the following:

Cu =40 g./l.

KCN =with 5 to 10 g./l. free KCN

Na_2CO_3 =100 g./l.

The electroplating is effected with the stainless steel wire as cathode at a current density of 10 a./dm.² and a temperature of 50° C.

EXAMPLE 5

The process of Example 4 is repeated, the wire however being finally electroplated in a bath containing the following:

Cu =40 g./l.

Zn =30 g./l.

KCN =3.5 concentration of $\text{Zn} \pm 0.2$

Na_2CO_3 =100 g./l.

The electroplating is effected with the stainless steel wire as cathode at a current density of 10 a./dm.² and a temperature of 40° C.

While the invention has been described with respect to certain preferred examples which give satisfactory results, it will be understood by those skilled in the art after understanding the principle of the invention, that various changes and modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. A process for the production of an electroplated stainless steel article which comprises activating the sur-

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face of a stainless steel substrate by cathodic treatment in an aqueous acid bath at a current density of not less than 10 a./dm.², and then electroplating said activated surface to provide the desired layer or layers of electroplate.

2. A process as claimed in claim 1, wherein the aqueous acid has a pH of less than about 4.

3. A process as claimed in claim 1, wherein the current density used for activation is at least 10 a./dm.².

4. A process as claimed in claim 1, wherein the current density is from 10 to 300 a./dm.².

5. A process as claimed in claim 1, wherein the anode used to effect the cathodic treatment of the stainless steel is of a material which does not release metal ions to the acid bath.

6. A process as claimed in claim 5, wherein the residence time of the article to be treated in the acid bath is from 0.1 second to 1 minute.

7. A process as claimed in claim 1, wherein the substrate treated is in the form of a wire, strip or sheet.

8. A process as claimed in claim 7, wherein the substrate is treated by continuous passage through the acid bath.

9. A process according to claim 8, wherein the electroplating is effected in an aqueous alkaline electroplating bath.

10. A process as claimed in claim 1, wherein the electroplating is effected in an aqueous acid electroplating bath.

11. A process as claimed in claim 10, wherein the electroplating is effected at a pH of not greater than 5.

12. A process as claimed in claim 10, wherein the electroplated layer comprises a metal selected from the group consisting of zinc, iron, cadmium, nickel, lead, manganese, copper, silver and gold.

13. A process as claimed in claim 1, wherein the electroplating is effected in an aqueous alkaline electroplating bath.

14. A process as claimed in claim 13, wherein the electroplated layer comprises copper.

15. A process as claimed in claim 13, wherein the electroplated layer comprises zinc.

16. A process as claimed in claim 1 wherein the cathodic treatment is effected in an aqueous solution of a mineral acid.

17. A process as claimed in claim 16 wherein the mineral acid is selected from the group consisting of H_2SO_4 , HCl , H_3PO_4 , HBF_4 , HF and $\text{NH}_2\text{SO}_3\text{H}$.

18. A process as claimed in claim 16, wherein the aqueous acid has a pH of less than about 4.

19. A process as claimed in claim 16, wherein the current density used for activation is at least 10 a./dm.².

20. A process as claimed in claim 1, wherein the substrate is subjected to a cleaning step before the cathodic treatment.

21. A process as claimed in claim 20, wherein the cleaning step is effected by anodic treatment in dilute aqueous solutions of hydrochloric, sulphuric or phosphoric acid.

22. A process as claimed in claim 21, wherein the anodic treatment is combined with an initial cleaning treatment comprising immersion of the substrate in an alkaline bath.

23. A process as claimed in claim 21, wherein the anodic treatment is effected for a period of from 0.1 seconds to 1 minute.

24. A process as claimed in claim 23, wherein the anodic treatment is combined with an initial cleaning treatment comprising immersion of the substrate in an alkaline bath.

25. A process as claimed in claim 21, wherein the anodic treatment is effected at a current density of from 1 to 100 a./dm.².

26. A process as claimed in claim 25, wherein the anodic treatment is effected for a period of from 0.1 second to 1 minute.

27. A process as claimed in claim 25, wherein the anodic treatment is combined with an initial cleaning

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treatment comprising immersion of the substrate in an alkaline bath.
28. Electroplated stainless steel articles constructed in accordance with the process of claim 1.

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