

1

2,728,720

## METHOD OF PRODUCING AN ELECTROPLATE OF NICKEL ON MAGNESIUM AND THE MAGNESIUM-BASE ALLOYS

Herbert K. De Long, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

No Drawing. Application March 9, 1953,  
Serial No. 341,377

3 Claims. (Cl. 204—32)

The invention relates to a method of producing an electroplate of nickel on articles of magnesium and the magnesium-base alloys.

Heretofore attempts to produce an electroplate of nickel on articles of magnesium and the magnesium-base alloys (that is, alloys in which the magnesium content exceeds 85 per cent by weight of the alloy) have been beset with many difficulties and the plates obtained leave much to be desired. One of the obstacles to the satisfactory electroplating of magnesium is that conventional nickel plating baths of the acid type either attack and corrode magnesium surfaces leaving them pitted or otherwise defaced, especially in recessed areas beyond the throwing power of the bath, or fail to yield satisfactory electroplates.

Because of the attack by conventional nickel plating baths on surfaces of magnesium and the magnesium-base alloys, especially on areas beyond the throwing power of the baths, it has been proposed to coat these areas with protective varnishes and the like so that the electroplating bath solution cannot come in direct contact with the areas on which electroplating does not occur. This procedure has the disadvantage of not only requiring extra steps in the electroplating procedure but also in some cases requires the further step of removal of the protective coating after the electroplating operation.

The principal object of the present invention is to provide a method of producing an electroplate of nickel upon articles of magnesium and the magnesium-base alloys which is not subject to the aforesaid disadvantages. Other objects and advantages will appear as the description of the invention proceeds.

In carrying out the invention, the articles to be nickel plated are first cleaned, if necessary, in any appropriate manner so as to remove visible foreign material as in conventional practice. Such cleaning operation forms no part of the present invention, the step of which now follows: The article to be plated, after having visible surface contaminants removed as just indicated, is subjected to a defilming operation for the removal of the invisible oxide and hydroxide layer always left on the surface after the usual cleaning operations. This may be accomplished by bathing the article in a dilute acidulated aqueous solution of a fluoride, such as one of the alkali metal or ammonium bifluorides. As an example of this, a solution may be made up of 100 grams of ammonium bifluoride plus 200 milliliters of 85 per cent of phosphoric acid ( $H_3PO_4$ ) in enough water to make one liter. Another example is a solution made of 400 milliliters of 50 per cent HF solution plus 10 milliliters of 70 per cent  $HNO_3$  solution in enough water to make one liter. The foregoing fluoride solutions on removing the oxide and hydroxide film from cleaned magnesium articles leave a coating of magnesium fluoride which protects the surface to be plated sufficiently from oxidation before the plating step begins.

The defilmed article is removed from the defilming bath and rinsed with water and then, without allowing

2

the rinsed surface to dry, the wet article is immersed in the plating bath and subjected to electrodeposition of nickel. The plating bath consists of an aqueous acidulated nickel bifluoride solution containing a polybasic acid, e. g. citric acid, tartaric acid, or the alkali earth metal salt of such acids, e. g. the calcium and magnesium salts. The plating bath may be prepared conveniently by mixing together in water nickel carbonate and hydrofluoric acid using enough of the acid to reduce the pH of the resulting solution to between 1 and 3 and then dissolving in the solution a suitable polybasic acid or alkali earth metal salt thereof. The following bath formulation is illustrative of this practice:

### Example

|                                                            | Grams |
|------------------------------------------------------------|-------|
| Nickel carbonate ( $NiCO_3$ or $2NiCO_3 \cdot 3Ni(OH)_2$ ) | 140   |
| Hydrofluoric acid (calculated as 100% HF)                  | 50    |
| Citric acid                                                | 30    |
| Water, enough to make up to 1 liter.                       |       |

Electroplating is carried out at elevated temperature by electrolyzing the plating solution using the articles to be plated as the cathode and an insoluble anode, such as carbon, or an anode of nickel. The temperature of the bath is critical and is maintained at 125° to 140° F. A sufficient voltage is applied to produce a current density at the surface of the articles to be plated of 30 to 100 amperes per square foot of article surface. During the plating, it is desirable to maintain the bath in a state of agitation or to keep the work in motion in the bath without stirring up any sediment which may form in the bath. After a sufficient thickness of electrodeposit is produced, the plated article is removed from the bath, rinsed, and dried preferably in a current of warm air.

As a measure of the non-corrosive characteristics of the plating bath, made up in accordance with the practice of the invention, test panels of a conventional magnesium-base alloy sheet were left immersed in the plating solution for a day, the panels being weighed before and after the immersion. In a test of this kind, a nickel plating bath was made up having the following composition:

|                                        | Oz. per gallon |
|----------------------------------------|----------------|
| $NiCO_3$                               | 18.7           |
| Citric acid                            | 4.6            |
| HF sufficient to reduce the pH to 3.0. |                |

A pair of test panels having an average area of 56.8 cm.<sup>2</sup> of a magnesium alloy composed nominally of 3 per cent Al, 1 per cent Zn, 0.3 per cent Mn, the balance being magnesium, was left immersed in the foregoing solution at room temperature for 24 hours with no loss in weight. For comparison, pairs of similar panels were left immersed to conventional nickel plating baths of the following compositions:

| Conventional bath No. 1: |                |
|--------------------------|----------------|
|                          | Oz. per gallon |
| $NiSO_4 \cdot 6H_2O$     | 40             |
| $NiCl_2 \cdot 6H_2O$     | 8              |
| $H_3BO_3$                | 5              |
| Conventional bath No. 2: |                |
| $NiCO_3$                 | 20             |
| $H_3BO_3$                | 4.6            |
| HF to reduce pH to 4.2.  |                |
| Conventional bath No. 3: |                |
| $NiSO_4 \cdot 6H_2O$     | 7.9            |
| $H_3BO_3$                | 4.6            |
| $NH_4HF_2$               | 6.8            |
| HF to reduce pH to 5.5.  |                |

3

The results of the immersions are tabulated below:

| Conventional Bath No. | Hours Du-<br>ration of<br>Immersion | Average of Two Panels   |                                   |
|-----------------------|-------------------------------------|-------------------------|-----------------------------------|
|                       |                                     | Grams<br>Weight<br>Lost | Loss,<br>Mg/cm. <sup>2</sup> /day |
| 1. ....               | 1                                   | 0.3978                  | 70.88                             |
| 2. ....               | 24                                  | 0.6878                  | 12.28                             |
| 3. ....               | 24                                  | 0.6127                  | 10.92                             |

From the foregoing data, it is manifest that the conventional nickel plating baths produce excessive corrosion on magnesium-base alloy articles while the improved bath of the invention produces no significant attack on the work.

Among the advantages of the invention are that portions of an article so deeply recessed as not to become plated while the unrecessed portions are being plated are not corroded by the plating bath; the plating operation can be conducted successfully over a wide range of current densities above those to which the conventional plating of magnesium articles is limited; the electroplates obtained are soft and ductile as compared to those conventionally produced; the electrodeposits are smooth and bright.

I claim:

1. The method of producing soft ductile electroplates of nickel on articles of magnesium and the magnesium-base alloys which comprises subjecting the articles to

4

the defilming action of a dilute acidulated aqueous solution of a fluoride selected from the group consisting of hydrogen fluoride, ammonium bifluoride, sodium bifluoride, potassium bifluoride, rinsing the defilmed articles in water, and without drying the rinsed articles electrolyzing the articles as cathodes in an electroplating bath consisting of an aqueous solution containing nickel bifluoride and hydrogen fluoride, said solution having a pH of 1 to 3 and containing per liter of the solution 10 to 50 grams of an organic polybasic acid compound selected from the group consisting of citric acid, tartaric acid, and the alkali earth metal salts of these acids.

2. The method according to claim 1 in which the temperature of the electroplating bath is 125° to 140° F.

3. The method according to claim 2 in which the current density at the surface of the articles is from 30 to 100 amperes per square foot.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

|           |                    |               |
|-----------|--------------------|---------------|
| 1,837,835 | Pinner et al. .... | Dec. 22, 1931 |
| 2,313,756 | Loose .....        | Mar. 16, 1943 |
| 2,436,690 | Du Rose .....      | Feb. 24, 1948 |
| 2,494,205 | Rogge et al. ....  | Jan. 10, 1950 |

#### OTHER REFERENCES

The Electrochemical Society, vol. 81, 1942, pages 213-230.